

A Reference Multiparameter Thermal Conductivity Equation for Carbon Dioxide with an Optimized Functional Form

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(Received 8 May 2006; accepted 9 May 2006; published online 16 October 2006)

A new thermal conductivity equation $\lambda = \lambda(T, \rho)$ in a multiparameter format was developed for carbon dioxide through the application of an optimization technique of the functional form. The proposed equation is valid for temperatures from the triple point ($T_t = 216.592$ K; $P_t = 0.51795$ MPa) to 1000 K and pressures up to 200 MPa. The calculation of density, which is an independent variable of the equation, from the experimental (T, P) conditions is performed with a high accuracy equation of state for the fluid. The thermal conductivity equation shows an average absolute deviation of 1.19% on the selected 1407 primary data points. Its performances are slightly better than those of the corresponding conventional model by Vesovic *et al.* [J. Phys. Chem. Ref. Data **19**, 763 (1990)] available from the literature; moreover the new equation is simpler to use in particular for the near-critical region. Tables of generated values of carbon dioxide thermal conductivity are provided for check of the code implementations and for quick evaluations. © 2006 American Institute of Physics. [DOI: 10.1063/1.2213631]

Key words: carbon dioxide; CO₂; multiparameter equations; thermal conductivity; transport properties correlation techniques.

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1. Nomenclature

Symbol	Description
\bar{a}	Array of individual coefficients
AAD	Average absolute deviation
Bias	Bias
g, h, n	Adjustable parameters
i	Index
M	Molar mass
MAD	Maximum average deviation
\bar{n}	Array of individual coefficients
N	Number of primary data
N_A	Avogadro number

Symbol	Description
NPT	Number of data
P	Pressure
R	Gas constant
T	Thermodynamic temperature
$u\%$	Ascribed uncertainty
Greek	
α	Function
χ^2	Sum of squares
Δ	Error deviation
λ	Thermal conductivity
Λ_c	Thermal conductivity reducing parameter
ρ	Mass density
Subscripts	
c	At the critical point
ce	Critical enhancement
calc	Calculated
exp	Experimental
i, j, k, l	Indexes
r	Reduced
t	At the triple point

2. Introduction

Carbon dioxide is a fluid with a wide scientific and technological interest. In particular, its industrial applications are becoming more and more important for instance as refrigerant fluid with low environmental impact, as supercritical solvent in extraction processes, and as enhancement agent for reservoir oil recovery.

The scientific importance of carbon dioxide is also related to the easiness for the experimenter to reach critical states, because the CO₂ critical temperature is not far from ambient temperature; in fact its critical point is located at $T_c=304.1282$ K and $P_c=7.3773$ MPa, as reported by Span and Wagner.¹ This substance is then regarded as test fluid for the application of theories of critical phenomena. Also the triple point ($T_t=216.592$ K, $P_t=0.51795$ MPa, from Span and Wagner¹) can be quite easily reached and in particular it is characterized by a pressure value greater than the atmospheric one. Moreover, carbon dioxide is important as a working fluid for calibration purposes.

Therefore the knowledge of thermodynamic and thermo-physical properties of CO₂ with the highest possible precision is a crucial need. A high accuracy fundamental equation of state (EoS) is available for CO₂,¹ from which all the thermodynamic properties can be calculated. The present work is instead addressed to the modeling of the thermal conductivity.

Several approaches for the representation of transport properties are published in the literature; a brief summary is

given in other works.^{2,3} Among different techniques, the method usually adopted for dedicated equations development is based on the residual concept: it considers each transport property function as composed of three parts, that are the zero-density term, the excess term, and the critical enhancement term.⁴ Empirical or theoretically founded equations are given for each term. In spite of the theoretical base of part of the model, the technique is however correlative and the development of the equation for the considered fluid requires experimental data of the transport property in the whole interest range. In the following the equations in this format will be referred to as "conventional."

The general form of the obtained thermal conductivity equation is $\lambda = \lambda(T, \rho)$, where the independent variables are the temperature T and the density ρ . Since the controlled variables for the experimentation and for the technical applications are the temperature T and the pressure P , an accurate EoS is needed for the calculation of the corresponding density value. This is a necessary condition for all the transport property equations covering the whole fluid surface, unless implicit functional forms are used.⁵

Some totally correlative techniques, alternative to the conventional procedure, were also developed.^{2,3,6-14} The technique for optimizing the functional form of multiparameter EoSs, set up by Setzmann and Wagner,¹⁵ has proved to be a powerful function approximator capable of drawing a transport property equation directly from the available experimental data. The method was previously used with successful results for the modeling of viscosity^{2,12,13} and of thermal conductivity.^{3,14} The present work deals with the application of this modeling technique to the representation of the thermal conductivity of carbon dioxide.

The thermal conductivity equation developed by Vesovic *et al.*¹⁶ in the conventional format and published in 1990 has been assumed here for comparison.

3. Experimental Data

Due to its scientific and technological interest, the carbon dioxide thermal conductivity was extensively studied in the last 70 years, so data sets from several researchers are found in the literature. However, in the last 20 years only few sources of precise data^{17,18} were published and were used also in the development of the Vesovic *et al.*¹⁶ equation, whereas more recent data¹⁹⁻²¹ are found to be rather inaccurate. The available data were measured with several experimental techniques, in some cases not completely well established, and the data sets have very different uncertainty levels.

The data sources in chronological order, grouped according to the described states (liquid, vapor, supercritical), are reported in Table 1. All over the present work, *liquid* refers to a thermodynamic condition with temperature lower than the critical temperature and pressure higher than the saturation pressure; *vapor* is characterized by pressure lower than the saturation pressure or, at temperatures above the critical temperature, by pressure lower than the critical pressure; *super-*

critical indicates that both temperature and pressure are higher than the respective critical values; *zero density* stands for vapor conditions extrapolated to the limit of zero density. The number of points (NPT) and the independent variables ranges of each data set are also reported. Where necessary, temperatures were converted to the International Temperature Scale of 1990 (ITS-90).⁷⁷

Table 1 reports also the result of the screening procedure described in Sec. 4.3, i.e., the final classification of the data sources as primary (I) or secondary (II). The estimated uncertainties used to determine the weighting factors for the primary data are given in the last column of the table.

The distribution of these primary data in the T, P plane is shown in Fig. 1 and a magnification for the region around the critical temperature is given in Fig. 2.

As it is evident from Table 1 and Figs. 1 and 2, the low-density vapor region and the near-critical region are thoroughly investigated, whereas the thermal conductivity in the liquid region and in the vapor region at higher temperatures and intermediate pressures is not as well documented.

4. Procedure for Heuristically Developing the New Equation for Thermal Conductivity

4.1. Fitting a Multiparameter Empirical Equation

The thermal conductivity surface of a fluid can be described through an empirical multiparameter equation in the form $\lambda = \lambda(T, \rho, \bar{n})$, where \bar{n} represents the array of the individual coefficients to be fitted. The optimum set of values for the equation coefficients \bar{n} is obtained by minimizing an objective function calculated as a weighted sum of squares

$$\chi^2(\bar{n}) = \sum_{i=1}^N \left(\frac{100 \lambda_{\text{exp}} - \lambda_{\text{calc}}(\bar{n})}{u\%} \right)_i^2 \quad (1)$$

where N is the total number of primary experimental data and $u\%$ is the estimated uncertainty of the point; the subscripts exp and calc stand for experimental and calculated values, respectively.

In Eq. (1) the data are weighted using their estimated experimental uncertainties $u\%$, so the contribution to the objective function resulting from the points with a larger experimental error is lower than for the more precise measurements. For the way the uncertainties were estimated see Sec. 4.3.

The algorithm developed by Setzmann and Wagner¹⁵ is the base of the optimization technique used for the present study. Given a bank of terms, i.e., a set of simple mathematical expressions whose summation is suitable to represent the desired functional dependence, the algorithm determines the functional form which yields the best representation of the selected experimental data with the lowest number of terms.

Since the Setzmann and Wagner algorithm is limited to equations linear in the coefficients \bar{n} , for the present problem the flexibility of the technique was increased by coupling also a nonlinear regression method. In this way the restric-

TABLE 1. Summary of the available thermal conductivity data sets for CO₂

Ref.	First author	Phase ^a	NPT	T range (K)	P range (MPa)	Meas. method ^b	Class	Uncert. (%)
Liquid								
22	Sellschopp	l	22	285–304	5.7–9.0	CC	I	5.0
23	Koch	l	18	283–303	5.1–9.1	HW, S	II	—
24	Borovik	l	9	283–303	5.1–9.1	CC	II	—
25	Keyes	l	1	274	5.8	CC	II	—
26	Guildner	l	4	277–299	4.5–7.7	CC	II	—
27	Michels	l	14	298–303	6.4–134.4	PP	I	2.0
28	Le Neindre	l	13	295–304	10.7–104.1	CC	I	5.0
29	Shingarev	l	17	231–303	5.8–20.3	HW, S	II	—
30	Le Neindre	l	6	296–304	21.1–81.1	CC	I	5.0
31	Tarzimanov	l	4	299	10.1–81.0	HW, S	II	—
32	Le Neindre	l	11	298	10.0–110.0	CC	I	5.0
33	Paul	l	5	298	6.6–30.7	HW	II	—
34	Salmanov	l	19	222–282	2.0–9.0	HW	I	5.0
35	Becker	l	19	298	6.6–40.1	I	II	—
36	Tarzimanov	l	12	297–304	9.0–196.0	HW, S	I	5.0
23	Koch	sl	8	283–303	*	HW, S	II	—
37	Amirkhanov	sl	90	293–303	*	CC, PP	II	—
Total		272						
Vapor								
38	Weber	zd	1	273	—	HW, S	II	—
39	Trautz	zd	1	273	—	HW, S	II	—
40	Dickins	zd	1	285	—	HW, S	I	1.0
41	Kannuluik	zd	1	273	—	HW, S	II	—
22	Sellschopp	v	18	285–314	0.1–6.7	CC	II	—
42	Archer	zd	11	285–592	—	HW, S	II	—
43	Sherratt	zd	10	339–566	—	HW, S	II	—
44	Eucken	zd	6	195–598	—	HW, S	II	—
23	Koch	v	32	283–313	0.1–7.1	HW, S	II	—
45	Johnston	zd	14	186–379	—	HW, S	I	1.0
46	Kannuluik	v	26	197–375	0.0–0.1	HW, S	II	—
24	Borovik	v	7	293–313	5.1–7.1	CC	II	—
25	Keyes	v	14	274–298	0.1–6.1	CC	II	—
47	Stops	zd	6	577–1308	—	HW, S	II	—
48	Kannuluik	v	9	275	0.0–0.1	CC	II	—
49	Stolyarov	v	12	280–475	0.1–3.0	HW, S	II	—
50	Franck	zd	7	197–598	—	HW, S	II	—
51	Keyes	zd	5	274–631	—	CC	I	5.0
52	Keyes	v	9	274–423	0.1–6.1	CC	II	—
53	Lenoir	v	12	314–340	0.1–6.8	CC	I	1.0
54	Rothman	v	29	631–1047	0.1	CC	II	—
55	Thomas	zd	4	314–337	—	HW, S	II	—
56	Salceanu	zd	1	303	—	HW, S	II	—
57	Guildner	v	4	304–305	0.2–7.3	CC	II	—
58	Vines	v	4	543–1173	0.1	CC	II	—
59	Geier	v	12	273–1373	0.1	CC	II	—
26	Guildner	v	12	277–347	0.2–5.8	CC	II	—
27	Michels	v	104	298–348	0.1–7.4	PP	I, II	2.0
60	Westenberg	zd	3	300–500	—	HW, S	II	—
28	Le Neindre	v	11	294–309	0.1–5.7	CC	II	—
61	Mukhopadhyay	v	7	258–473	0.1	HW, S	II	—
62	Barua	zd	5	273–473	—	HW, S	II	—
63	Christensen	zd	3	308–388	—	HW, S	II	—
29	Shingarev	v	2	299–307	1.0	HW, S	II	—

TABLE 1. Summary of the available thermal conductivity data sets for CO₂—Continued

Ref.	First author	Phase ^a	NPT	T range (K)	P range (MPa)	Meas. method ^b	Class	Uncert. (%)
64	van Dael	v	1	297	0.1	HW, S	II	—
30	Le Neindre	v	112	327–961	0.1–7.1	CC	I, II	5.0
65	Rosenbaum	v	8	336–434	3.3–7.1	CC	II	—
66	Gupta	v	98	373–1348	0.0–0.1	HW, S	II	—
67	Murthy	v	2	305–308	0.2	PP	II	—
31	Tarzimanov	v	8	299–581	0.1–6.5	HW, S	II	—
32	Le Neindre	v	37	298–951	0.1	CC	II	—
68	Haarman	zd	8	328–468	—	HW, S	II	—
33	Paul	v	12	298–313	0.7–6.9	HW	II	—
69	Shashkov	zd	9	315–403	—	HW	II	—
70	Bakulin	v	28	225–316	0.1–2.0	HW, S	I	5.0
71	Bakulin	v	10	400–1300	0.1	HW, S	I	5.0
35	Becker	v	28	298–308	3.1–7.4	I	II	—
36	Tarzimanov	v	12	290–654	0.1–6.1	HW, S	II	—
72	Clifford	v	22	301–304	0.6–5.9	HW, T	I	0.5
73	Snel	v	133	298–323	0.0–5.5	HW, S	I	1.5
74	Scott	v	42	301–350	0.3–6.8	HW, T	I	0.5
17	Johns	v	14	381–474	1.8–7.2	HW, T	I	0.5
18	Millat	v	91	305–426	0.4–6.7	HW, T	I	0.5
19	Chen	v	19	304–316	1.4–7.4	TM	II	—
20	Dohrn	v	7	300–420	0.1	HW, T	II	—
21	Heinemann	v	3	323–420	0.1	HW, T	II	—
23	Koch	sv	9	279–303	*	HW, S	II	—
Total			1116					
Supercritical region								
22	Sellschopp	sc	10	304–323	7.5–9.1	CC	II	—
23	Koch	sc	4	308–313	8.1–9.1	HW, S	II	—
24	Borovik	sc	2	313	8.1–9.1	CC	II	—
49	Stolyarov	sc	23	326–473	10.1–30.4	HW, S	II	—
53	Lenoir	sc	20	314–340	8.0–20.8	CC	II	—
57	Guildner	sc	18	305–348	7.5–30.4	CC	II	—
26	Guildner	sc	1	304	7.9	CC	II	—
27	Michels	sc	136	304–348	7.4–209.7	PP	I	2.0
28	Le Neindre	sc	7	305–306	13.1–68.8	CC	I	5.0
29	Shingarev	sc	4	310–326	19.9–20.0	HW, S	II	—
30	Le Neindre	sc	407	304–961	7.6–127.8	CC	I	5.0
65	Rosenbaum	sc	42	336–434	10.0–69.0	CC	II	—
75	Murthy	sc	53	305–310	7.5–8.3	PP	II	—
67	Murthy	sc	1	308	8.3	PP	II	—
31	Tarzimanov	sc	53	379–678	10.1–101.3	HW, S	II	—
32	Le Neindre	sc	146	327–951	10.0–120.0	CC	I	5.0
76	Murthy	sc	65	305–310	7.5–8.3	PP	II	—
33	Paul	sc	4	313	9.1–27.6	HW	II	—
35	Becker	sc	170	304–308	7.4–48.8	I	II	—
36	Tarzimanov	sc	70	305–678	9.8–196.0	HW, S	I	5.0
74	Scott	sc	50	315–348	7.4–24.6	HW, T	I	0.5
17	Johns	sc	33	381–473	7.4–30.6	HW, T	I	0.5
19	Chen	sc	47	304–316	7.4–13.1	TM	II	—
Total			1366					
Overall								
Overall			2754					

^aPhase: l=liquid phase; sl=saturated liquid; v=vapor phase; sv=saturated vapor; zd=zero density; sc=supercritical region.^bMeasurement method: CC=concentric cylinder; HW=hot wire; HW, S=hot wire steady-state; HW, T=hot wire transient; I=interferometry; PP=parallel plate; TM=thermoelectric module.

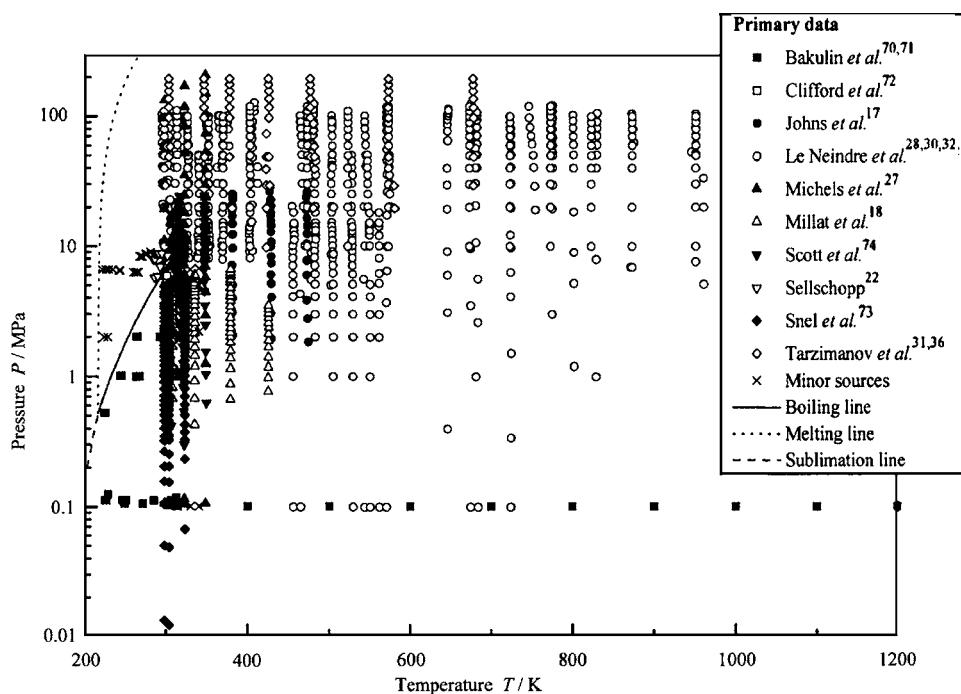


FIG. 1. Distribution of the experimental points selected as primary data.

tions imposed by the linear method was overcome. The details of the fitting procedure are described at Sec 4.3.

4.2. Bank of Terms

A bank of terms including a total of 285 terms was used for the optimization of the functional form. According to this choice, the most general form of the thermal conductivity equation can be written as

$$\lambda_r(T_r, \rho_r, \bar{n}, \bar{a}) = \sum_{i=0}^{12} \sum_{j=0}^{10} n_{ij} T_r^{i/2} \rho_r^j + e^{-5\rho_r^2} \cdot \sum_{k=0}^{12} \sum_{l=0}^{10} n_{kl} T_r^{k/2} \rho_r^l + n_c \lambda_{r,ce}(T_r, \rho_r, \bar{a}) \quad (2)$$

with $j \neq 0$ when $i=0$, and $l \neq 0$ when $k=0$.

The reduced variables in Eq. (2) are defined as

$$T_r = T/T_c,$$

$$\rho_r = \rho/\rho_c,$$

$$\lambda_r = \lambda/\Lambda_c. \quad (3)$$

For temperature and density the corresponding critical values are used as reducing parameters, but the same is not possible for thermal conductivity because this property becomes infinite at the critical point,⁷⁸ so a “critical thermal conductivity” cannot be measured. A parameter derived from the dimensional analysis is therefore adopted, as it was done in former cases such as by Laesecke *et al.*:⁵

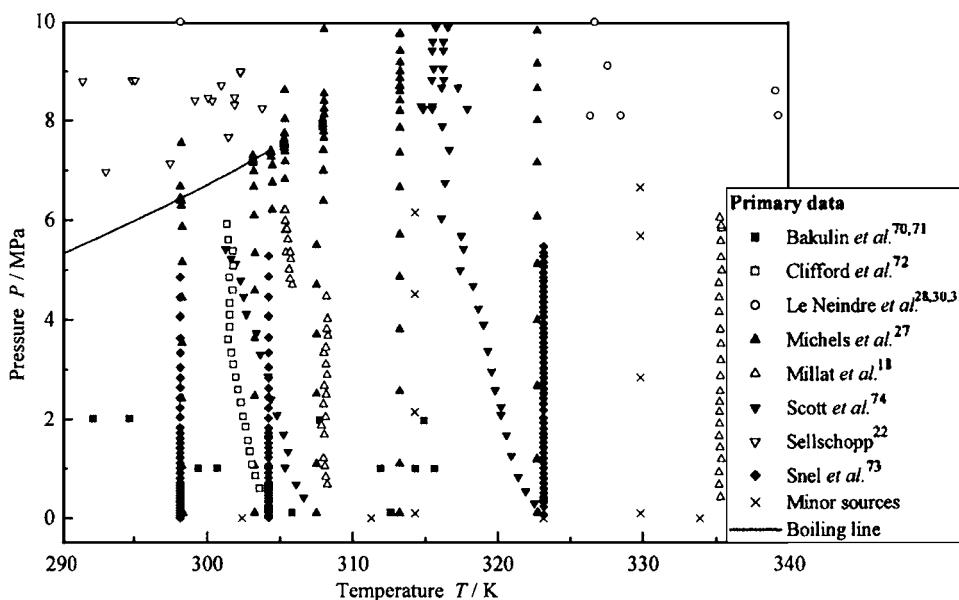


FIG. 2. Distribution of the primary data around the critical temperature.

TABLE 2. Substance-specific parameters for the target fluid CO₂

		Reference
M (kg mol ⁻¹)	0.044098	1
T_c (K)	304.1282	1
P_c (MPa)	7.3773	1
ρ_c (kg m ⁻³)	467.6	1
Λ_c (mW m ⁻¹ K ⁻¹)	4.81384	—

$$\Lambda_c = \frac{R^{5/6} P_c^{2/3}}{T_c^{1/6} M^{1/2} N_A^{1/3}}. \quad (4)$$

For carbon dioxide the values of the parameters involved in the former variable definitions are reported in Table 2 to-

gether with the literature reference.

Further parameters are the molar gas constant ($R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$) as given by Mohr and Taylor,⁷⁹ and the Avogadro's number ($N_A = 6.0221353 \times 10^{23} \text{ mol}^{-1}$) as given by Becker *et al.*⁸⁰

Excluding the term $\lambda_{r,ce}$, the present bank of terms, Eq. (2), is similar to that successfully set up for the development of equations for thermodynamic properties^{81,82} and for viscosity^{2,12,13} of pure fluids. Some preliminary tests have shown that it is suitable to represent the background thermal conductivity of a pure fluid. The representation of the thermal conductivity enhancement in the near-critical region relies on the critical term $\lambda_{r,ce}$ reading:

$$\lambda_{r,ce}(T_r, \rho_r, \bar{a}) = \frac{\rho_r \exp\left\{-\frac{\rho_r^{a_1}}{a_1} - [a_2(T_r - 1)]^2 - [a_3(\rho_r - 1)]^2\right\}}{\left(\left[\left\{1 - \frac{1}{T_r}\right\} + a_4[(\rho_r - 1)^2]^{1/2a_5}\right]^2\right)^{a_6} + \{[a_7(\rho_r - \alpha)]^2\}^{a_8}} \quad (5)$$

in which it is

$$\alpha = \alpha(T_r) = 1 - a_{10} \operatorname{arccosh}\{1 + a_{11}[(1 - T_r)^2]^{a_{12}}\}. \quad (6)$$

The functional form in Eq. (5) was empirically obtained with a trial-and-error procedure on generated data of different fluids; it is sufficiently flexible to follow the trends of the data, as it was also shown by the results obtained for the fluids R134a³ and R152a.¹⁴ The parameters \bar{a} and the multiplying coefficient n_c are regressed on data of the target fluid during the fitting procedure.

As required by the thermal conductivity behavior, the functional form given by Eqs. (5) and (6) diverges to infinity at the critical point, it is identically null at zero-density conditions, and its numerical value decreases moving away from the critical point with a rate depending on the \bar{a} parameters.

The purpose of the α function is to allow the $\lambda_{r,ce}$ term to assume, along isotherms at temperatures higher than the critical one, a maximum value at densities different from the critical one, following the trend shown by the experimental data. The α function makes Eq. (5) nonsymmetric with respect to critical density.

The coefficients a_4 and a_5 , similarly to the corresponding parameters of the nonanalytical terms for the EoS development,⁸² should be fitted to density data of both saturated vapor and saturated liquid in the vicinity of the critical point. In this work these coefficients were fitted in such a way using density values at the saturation condition generated by the Span and Wagner EoS;¹ the obtained coefficients were then rounded to proper values with only two decimal digits.

It was chosen to include in the bank of terms a single but

very flexible critical enhancement term instead of several simpler terms with different values of the parameters; the choice is justified by the need for avoiding unreasonable interactions among the terms when more than one of them would be selected for the equation during the fitting procedure. The obtained results show that one single term with the form of Eq. (5) is sufficient to satisfactorily represent the critical enhancement part of the thermal conductivity.

4.3. Screening of Data and Fitting Procedure

The experimental data sets available from the literature cannot be used as a whole in the fitting procedure because of their different uncertainty levels and the possible presence of systematic errors. They then have to undergo a screening procedure with the goal of identifying the more precise data sources to include in the final regression; these experimental points are called *primary data*. The rejected sources compose the *secondary data*, that are used only for comparison.

The adopted modeling technique, being heuristic, can be used for this purpose. The screening and the fitting are performed at the same time through a series of steps according to the exposed procedure. The statistical indexes defined in Eq. (9) are used to evaluate the deviations of the data sets from the correlation.

The first choice of primary data was done considering the same data sets used in the development of the conventional equation of Vesovic *et al.*¹⁶ (i.e., the data of Johns *et al.*,¹⁷ Millat *et al.*,¹⁸ Michels *et al.*,²⁷ Le Neindre *et al.*,^{28,30,32} Dickins,⁴⁰ Johnston and Grilly,⁴⁵ Franck,⁵⁰ Keyes,⁵¹ Lenoir and Comings,⁵³ Clifford *et al.*,⁷² Snel *et al.*,⁷³ and Scott *et*

TABLE 3. Parameters of Eq. (7)

<i>i</i>	<i>g_i</i>	<i>h_i</i>	<i>n_i</i>	<i>i</i>	<i>g_i</i>	<i>h_i</i>	
1	0.0	1.0	7.69857587	7	1.5	5.0	22.3205514
2	0.0	5.0	0.159885811	8	1.5	9.0	66.1420950
3	1.5	1.0	1.56918621	9	3.5	0.0	-0.171779133
4	0.0	1.0	-6.73400790	10	5.5	0.0	0.00433043347
5	1.0	2.0	16.3890156				
6	1.5	0.0	3.69415242	<i>n_c</i>			0.775547504

al.⁷⁴). The same values of experimental uncertainty adopted by Vesovic *et al.* were assumed for weighting the data in the objective function, Eq. (1). All the points of each of these data sets were included as primary data, supposing that, apart from evident outliers, all the data from the same source had been obtained with a rather homogeneous accuracy. It should be noted that no significant experimental source has been published after the development of the conventional equation; in fact the most recent data sets^{19–21} either present a limited number of points or show a low accuracy level with respect to the other sets. Therefore, the analysis of the data sources done by Vesovic *et al.*¹⁶ can be exploited here as well.

A first correlation was regressed with the optimization algorithm based on these data, considering only those falling outside the near-critical region. In this first step the critical term $\lambda_{r,ce}$ was excluded from the bank of terms.

The deviations of the experimental data from the obtained preliminary equation were calculated. It was evidenced that the data of Franck⁵⁰ have a lower accuracy compared to the other sources and this set was then moved to secondary data. Moreover, the three data sets of Le Neindre *et al.*^{28,30,32} in the vapor phase showed inconsistencies and systematic shifting with respect to the other data sets. From the three data sets of Le Neindre *et al.* in the vapor phase, it was decided to consider as primary data only the points of Le Neindre *et al.*³⁰ that cover the sparsely investigated regions, i.e., for temperatures greater than 450 K.

After a new regression on the modified set of primary data it was found that some secondary data sets in regions with few primary experimental data show deviations from the equation with an acceptable level. These are the data in the liquid region from Sellschopp²² and from Salmanov and Tarzimanov,³⁴ the vapor phase data from Bakulin *et al.*,^{70,71} and the data from Tarzimanov and Arslanov³⁶ for the liquid and supercritical regions. These data sets were included in

TABLE 4. Parameters of the critical term, Eqs. (5) and (6)

<i>i</i>	<i>a_i</i>	<i>i</i>	<i>a_i</i>
1	3.0	7	0.33791
2	6.70697	8	0.77963
3	0.94604	9	0.79857
4	0.30	10	0.90
5	0.30	11	0.02
6	0.39751	12	0.20

TABLE 5. Validity limits of Eq. (7)

<i>T</i> (K)	216.59–1000
<i>P</i> (MPa)	≤ 200

the set of the primary sources assuming an uncertainty of 5% and a new equation was obtained using the optimization algorithm.

After the foregoing steps, the primary data *inside* the near-critical region were also considered and the critical term $\lambda_{r,ce}$ with tentative \bar{a} coefficients was added to the last equation obtained in the previous part. A nonlinear regression method was used to fit only the coefficients \bar{n} and \bar{a} . It was found that the vapor phase data from Michels *et al.*²⁷ indicated as “near the coexistence line” in the original paper, have a lower quality compared to the other ones from the same source and these data were consequently excluded from the set of primary data. A new nonlinear regression was then done.

At this point the term $\lambda_{r,ce}$ with the last obtained coefficients \bar{n} and \bar{a} , was included again in the bank of terms and a few cycles, consisting of the Setzmann and Wagner algorithm¹⁵ followed by the nonlinear regression, were performed, each time updating the \bar{a} coefficients of $\lambda_{r,ce}$ in the bank of terms. The cycles were stopped when convergence was reached, i.e., when the equation coefficients remained substantially constant.

In Table 1 the primary data sets are indicated by the symbol I, while the secondary ones are labeled as II. For the primary data the uncertainties used in the evaluation of the objective function, Eq. (1), are reported in the last column of the table.

5. The New Thermal Conductivity Equation for Carbon Dioxide

5.1. Recommended Equation of State

As usual, the independent variables of the proposed thermal conductivity equation are temperature and density, whereas the variables that can be controlled in the experimentation and in the technical applications are temperature and pressure. Therefore an EoS is needed to convert the variables from (T, P) into (T, ρ) . The very accurate equation from Span and Wagner¹ was assumed in the present work and it was used to calculate the density of each experimental point, given T and P , and to transform the thermal diffusivity measurements of Becker and Grigull³⁵ into thermal conductivity values. The same EoS¹ should be used when calculating values from the new thermal conductivity equation as a function of temperature and pressure.

5.2. The Multiparameter Equation

Once the final choice of primary data sets had been done, the new thermal conductivity equation in the form $\lambda = \lambda(T, \rho)$ was obtained at the end of the fitting procedure described in Sec. 4.3:

TABLE 6. Deviations of the new thermal conductivity equation, Eq. (7), with respect to primary, secondary, and overall data in liquid, vapor, and supercritical regions. Data are within the Eq. (7) validity limits.

Ref.	First author	Phase	NPT	T range (K)	P range (MPa)	Meas. method	AAD (%)	Bias (%)	MAD (%)	Class
Liquid phase										
22	Sellschopp	l	22	285–304	5.7–9.0	CC	1.30	-0.68	4.30	I
27	Michels	l	14	298–303	6.4–134.4	PP	1.38	-0.32	3.12	I
28	Le Neindre	l	13	295–304	10.7–104.1	CC	0.91	0.91	1.80	I
30	Le Neindre	l	6	296–304	21.1–81.1	CC	0.39	-0.08	1.04	I
32	Le Neindre	l	10	298	10.0–110.0	CC	0.52	-0.29	0.91	I
34	Salmanov	l	19	222–282	2.0–9.0	HW	1.54	1.47	2.12	I
36	Tarzmanov	l	11	297–304	29.4–196.0	HW, S	0.80	0.23	1.71	I
Primary			95					1.11	0.20	
23	Koch	l	18	283–303	5.1–9.1	HW, S	1.11	-1.09	3.48	II
24	Borovik	l	9	283–303	5.1–9.1	CC	2.65	-2.63	6.41	II
25	Keyes	l	1	274	5.8	CC	1.91	-1.91	1.91	II
26	Guildner	l	4	277–299	4.5–7.7	CC	2.41	2.41	3.36	II
29	Shingarev	l	17	231–303	5.8–20.3	HW, S	3.47	-1.26	11.28	II
31	Tarzmanov	l	4	299	10.1–81.0	HW, S	1.06	-0.99	1.77	II
33	Paul	l	5	298	6.6–30.7	HW	1.83	1.83	3.75	II
35	Becker	l	19	298	6.6–40.1	I	1.98	1.21	5.75	II
23	Koch	sl	8	283–303	*	HW, S	6.50	-4.78	32.38	II
37	Amirkhanov	sl	90	293–303	*	CC, PP	8.60	-6.72	46.36	II
Total			270					4.06	-2.42	
Vapor phase										
40	Dickins	zd	1	285	—	HW, S	0.23	-0.23	0.23	I
45	Johnston	zd	12	216–379	—	HW, S	0.65	0.65	1.82	I
51	Keyes	zd	5	274–631	—	CC	1.59	0.97	4.24	I
53	Lenoir	v	12	314–340	0.1–6.8	CC	1.27	1.24	3.83	I
27	Michels	v	71	298–348	0.1–7.4	PP	1.33	0.57	4.75	I
30	Le Neindre	v	70	456–961	0.1–7.1	CC	2.85	-2.64	6.26	I
70	Bakulin	v	28	225–316	0.1–2.0	HW, S	1.68	1.45	7.46	I
71	Bakulin	v	7	400–1000	0.1	HW, S	0.69	-0.12	1.46	I
72	Clifford	v	22	301–304	0.6–5.9	HW, T	0.83	0.81	2.77	I
73	Snel	v	133	298–323	0.0–5.5	HW, S	0.92	-0.81	2.03	I
74	Scott	v	42	301–350	0.3–6.8	HW, T	0.65	-0.50	1.60	I
17	Johns	v	14	381–474	1.8–7.2	HW, T	0.40	-0.03	0.90	I
18	Millat	v	91	305–426	0.4–6.7	HW, T	0.50	0.18	3.37	I
Primary			508					1.17	-0.33	
38	Weber	zd	1	273	—	HW, S	1.56	-1.56	1.56	II
39	Trautz	zd	1	273	—	HW, S	3.25	-3.25	3.25	II
41	Kannuluik	zd	1	273	—	HW, S	1.59	-1.59	1.59	II
22	Sellschopp	v	18	285–314	0.1–6.7	CC	7.01	-7.01	14.18	II
42	Archer	zd	11	285–592	—	HW, S	7.12	-7.12	11.13	II
43	Sherratt	zd	10	339–566	—	HW, S	1.75	1.48	4.48	II
44	Eucken	zd	5	273–598	—	HW, S	6.75	-6.75	9.38	II
23	Koch	v	32	283–313	0.1–7.1	HW, S	5.91	-5.91	34.75	II
46	Kannuluik	v	15	275–375	0.0–0.1	HW, S	1.83	1.76	4.70	II
24	Borovik	v	7	293–313	5.1–7.1	CC	10.26	-10.26	41.98	II
25	Keyes	v	14	274–298	0.1–6.1	CC	7.66	7.66	20.20	II
47	Stops	zd	4	577–912	—	HW, S	3.05	-1.75	8.48	II
48	Kannuluik	v	9	275	0.0–0.1	CC	2.06	-2.06	3.60	II
49	Stolyarov	v	12	280–475	0.1–3.0	HW, S	4.64	2.61	13.04	II
50	Franck	zd	6	276–598	—	HW, S	6.27	-6.27	8.55	II
52	Keyes	v	9	274–423	0.1–6.1	CC	2.43	1.44	7.14	II

TABLE 6. Deviations of the new thermal conductivity equation, Eq. (7), with respect to primary, secondary, and overall data in liquid, vapor, and supercritical regions. Data are within the Eq. (7) validity limits.—Continued

Ref.	First author	Phase	NPT	T range (K)	P range (MPa)	Meas. method	AAD (%)	Bias (%)	MAD (%)	Class
54	Rothman	v	23	631–961	0.1	CC	3.82	-2.46	7.52	II
55	Thomas	zd	4	314–337	—	HW, S	1.33	-1.33	1.49	II
56	Salceanu	zd	1	303	—	HW, S	6.01	-6.01	6.01	II
57	Guildner	v	4	304–305	0.2–7.3	CC	1.33	-0.90	2.38	II
58	Vines	v	2	543–823	0.1	CC	1.95	1.95	2.32	II
59	Geier	v	8	273–973	0.1	CC	1.71	-0.08	2.34	II
26	Guildner	v	12	277–347	0.2–5.8	CC	1.99	-0.89	5.78	II
27	Michels	v	33	298–303	6.4–7.2	PP	14.40	13.94	59.17	II
60	Westenberg	zd	3	300–500	—	HW, S	1.57	-1.57	2.03	II
28	Le Neindre	v	11	294–309	0.1–5.7	CC	0.68	-0.10	1.45	II
61	Mukhopadhyay	v	7	258–473	0.1	HW, S	1.90	-0.82	4.79	II
62	Barua	zd	5	273–473	—	HW, S	2.61	-2.10	4.95	II
63	Christensen	zd	3	308–388	—	HW, S	1.53	-1.53	1.72	II
29	Shingarev	v	2	299–307	1.0	HW, S	2.04	-2.04	2.58	II
64	van Dael	v	1	297	0.1	HW, S	1.05	-1.05	1.05	II
30	Le Neindre	v	42	327–406	0.1–7.1	CC	2.33	-2.10	5.02	II
65	Rosenbaum	v	8	336–434	3.3–7.1	CC	1.07	-1.03	2.72	II
66	Gupta	v	63	373–973	0.0–0.1	HW, S	4.26	-4.26	8.72	II
67	Murthy	v	2	305–308	0.2	PP	0.59	0.37	0.96	II
31	Tarzimanov	v	8	299–581	0.1–6.5	HW, S	2.16	-2.16	3.92	II
32	Le Neindre	v	37	298–951	0.1	CC	2.54	-1.69	5.02	II
68	Haarman	zd	8	328–468	—	HW, S	0.48	-0.48	0.62	II
33	Paul	v	12	298–313	0.7–6.9	HW	1.80	0.39	6.46	II
69	Shashkov	zd	9	315–403	—	HW	1.21	-0.87	3.05	II
35	Becker	v	27	298–308	4.1–7.4	I	5.97	-5.83	15.69	II
36	Tarzimanov	v	12	290–654	0.1–6.1	HW, S	4.15	3.37	10.53	II
19	Chen	v	19	304–316	1.4–7.4	TM, S	20.74	15.10	38.24	II
20	Dohrn	v	7	300–420	0.1	HW, T	4.18	4.18	5.47	II
21	Heinemann	v	3	323–420	0.1	HW, T	4.40	4.40	5.38	II
23	Koch	sv	9	279–303	*	HW, S	24.11	-23.29	95.99	II
Total			1048				3.30	-0.62		
Supercritical region										
27	Michels	sc	94	304–348	7.4–209.7	PP	1.22	-0.82	4.37	I
28	Le Neindre	sc	7	305–306	13.1–68.8	CC	0.77	0.72	1.89	I
30	Le Neindre	sc	405	304–961	7.6–127.8	CC	1.21	-0.48	6.41	I
32	Le Neindre	sc	145	327–951	10.0–120.0	CC	1.03	-0.25	3.90	I
36	Tarzimanov	sc	70	305–678	9.8–196.0	HW, S	1.87	0.93	4.68	I
74	Scott	sc	50	315–348	7.4–24.6	HW, T	1.15	0.69	6.30	I
17	Johns	sc	33	381–473	7.4–30.6	HW, T	0.76	0.10	4.65	I
Primary			804				1.21	-0.25		
22	Sellschopp	sc	10	304–323	7.5–9.1	CC	14.04	10.07	30.07	II
23	Koch	sc	4	308–313	8.1–9.1	HW, S	40.41	-40.41	102.35	II
24	Borovik	sc	2	313	8.1–9.1	CC	27.38	-27.38	31.77	II
49	Stolyarov	sc	23	326–473	10.1–30.4	HW, S	7.71	1.89	20.26	II
53	Lenoir	sc	20	314–340	8.0–20.8	CC	4.65	4.64	9.06	II
57	Guildner	sc	18	305–348	7.5–30.4	CC	12.16	11.01	51.60	II
26	Guildner	sc	1	304	7.9	CC	3.55	3.55	3.55	II
29	Shingarev	sc	4	310–326	19.9–20.0	HW, S	9.82	-9.82	19.02	II
65	Rosenbaum	sc	42	336–434	10.0–69.0	CC	2.83	0.13	13.24	II
75	Murthy	sc	53	305–310	7.5–8.3	PP	16.96	12.95	42.27	II
67	Murthy	sc	1	308	8.3	PP	0.91	0.91	0.91	II
31	Tarzimanov	sc	53	379–678	10.1–101.3	HW, S	2.25	-2.06	5.05	II
76	Murthy	sc	65	305–310	7.5–8.3	PP	13.99	10.72	42.27	II

TABLE 6. Deviations of the new thermal conductivity equation, Eq. (7), with respect to primary, secondary, and overall data in liquid, vapor, and supercritical regions. Data are within the Eq. (7) validity limits.—Continued

Ref.	First author	Phase	NPT	T range (K)	P range (MPa)	Meas. method	AAD (%)	Bias (%)	MAD (%)	Class
33	Paul	sc	4	313	9.1–27.6	HW	0.78	-0.29	1.69	II
35	Becker	sc	170	304–308	7.4–48.8	I	9.49	-1.39	54.76	II
19	Chen	sc	47	304–316	7.4–13.1	TM	27.04	25.26	74.05	II
Total			1321				5.15	1.67		
Overall										
Primary			1407				1.19	-0.25		
Total			2639				4.31	0.35		

$$\lambda_r(T_r, \rho_r) = \sum_{i=1}^3 n_i T_r^{g_i} \rho_r^{h_i} + e^{-5\rho_r^2} \sum_{i=4}^{10} n_i T_r^{g_i} \rho_r^{h_i} + n_c \lambda_{r,ce}(T_r, \rho_r) \quad (7)$$

The coefficients of this equation are reported in Table 3. In Eq. (7) the term $\lambda_{r,ce}(T_r, \rho_r)$ is given by Eqs. (5) and (6) with the parameters from Table 4. In Table 5 the validity limits of the proposed equation are reported. The extrapolation of the equation far outside these validity limits, particularly at low temperatures and at high pressures, should be avoided because it may result in rather unreliable calculated values.

As shown in Fig. 1 the primary data do not regularly fill all the extension of the stated validity range, however a regular contour was assumed for it. This assumption will be discussed further on in Sec. 5.5.

5.3. Validation of the New Thermal Conductivity Equation

A detailed comparison of the new thermal conductivity equation with both primary and secondary data is reported in this section.

Through all the present work the error deviation Δ was calculated as:

$$\Delta = \frac{\lambda_{\text{exp}} - \lambda_{\text{calc}}}{\lambda_{\text{exp}}} \quad (8)$$

TABLE 7. Deviations of the new thermal conductivity equation, Eq. (7), with respect to primary and secondary data in vapor with temperatures lower than the CO₂ triple point

Ref.	First author	Phase	NPT	T range (K)	P range (MPa)	Meas. method	AAD (%)	Bias (%)	MAD (%)	Class
45	Johnston	zd	2	186–201	—	HW,S	2.75	2.75	3.34	I
Primary			2				2.75	2.75		
44	Eucken	zd	1	195	—	HW,S	5.46	5.86	5.86	II
46	Kannuluik	v	11	197	0.0–0.1	HW,S	4.18	-3.36	8.67	II
50	Franck	v	1	197	0.0	HW,S	1.97	1.97	1.97	II
Total			15				3.93	-1.60		

From the error deviation Δ the following statistical quantities are evaluated: the average absolute deviation (AAD), the bias (Bias), and the maximum absolute deviation (MAD). These are calculated according to:

$$\text{AAD}(\%) = \frac{100}{\text{NPT}} \sum_{i=1}^{\text{NPT}} |\Delta|_i$$

$$\text{Bias}(\%) = \frac{100}{\text{NPT}} \sum_{i=1}^{\text{NPT}} (\Delta)_i$$

$$\text{MAD}(\%) = 100 \max_{i=1, \dots, \text{NPT}} (|\Delta|_i). \quad (9)$$

Table 6 presents the deviations of the equation from the available experimental data inside the validity limits indicated in Table 5. Some of the primary data sets in vapor phase contain experimental points at temperatures outside the validity limits, but they were chosen to include also these points in the regression in order to improve the extrapolation capability of the obtained equation. Also data belonging to secondary sources can be found outside the range. Comparisons of the equation with data outside its validity limits are reported in Table 7 for temperatures lower than the triple point and in Table 8 for higher temperatures.

The representation of the deviations of the new thermal

TABLE 8. Deviations of the new thermal conductivity equation, Eq. (7), with respect to primary and secondary data in vapor with temperatures higher than the Eq. (7) validity limits

Ref.	First author	Phase	NPT	T range (K)	P range (MPa)	Meas. method	AAD (%)	Bias (%)	MAD (%)	Class
71	Bakulin	v	3	1100–1300	0.1	HW,S	1.63	0.27	2.03	I
Primary				3				1.63	0.27	
47	Stops	zd	2	1203–1308	—	HW,S	2.61	-2.61	4.64	II
58	Vines	v	2	1033–1173	0.1	CC	5.72	5.72	5.72	II
54	Rothman	v	2	1042–1045	0.1	CC	2.64	2.64	3.16	II
59	Geier	v	4	1073–1373	0.1	CC	3.67	-3.67	8.50	II
66	Gupta	v	35	1073–1348	0.0–0.1	HW,S	1.25	-0.39	4.28	II
Total				48				1.78	-0.33	

conductivity equation with respect to all primary data is shown in Fig. 3 and a magnification of the same plot for the near-critical region is given in Fig. 4.

Deviations from primary data in the low-density region, here defined by $P < 0.12$ MPa, are presented in detail in Fig. 5. Furthermore, the deviations of Eq. (7) with respect to the experimental points of the primary data sets are shown in Fig. 6 as a function of pressure for several intervals of temperature. The dashed-dotted lines represent the deviation of data calculated by the conventional equation of Vesovic *et al.*¹⁶ from the new equation; for each figure the comparison temperature for the two equations was taken at the mean value of the indicated range.

The tables and figures discussed above show the satisfactory performance of the new thermal conductivity equation for CO₂. The observed deviations of primary data from the equation correspond to the claimed experimental uncertainties in each of the three regions. The significant values of bias are probably due to systematic shifting among different primary data sets.

Larger deviations of the data from the equation are located

in the region at high temperatures and for the points at pressures higher than 100 MPa, where less accurate data sets are available. Also the data for the low-density region show a strong scattering and some inconsistencies, but the equation results in a good balance between them.

The equation can safely be used for low-density vapor at temperatures outside the validity limits, even if at lower temperatures the deviations of the equation from the few available data are larger.

Table 6 shows that several experimental data sets, belonging to secondary sources, are affected by high systematic errors, particularly in vapor and supercritical regions.

5.4. Behavior of the Thermal Conductivity Surface

The obtained thermal conductivity equation is plotted on a λ, ρ plane for some isotherms and isobars in Fig. 7. In the same plot there is also a magnification for the liquid and supercritical regions at high pressures. The representation of the surface is regular, confirming the reliability of the new equation. The steep trends of the vapor and liquid lines at

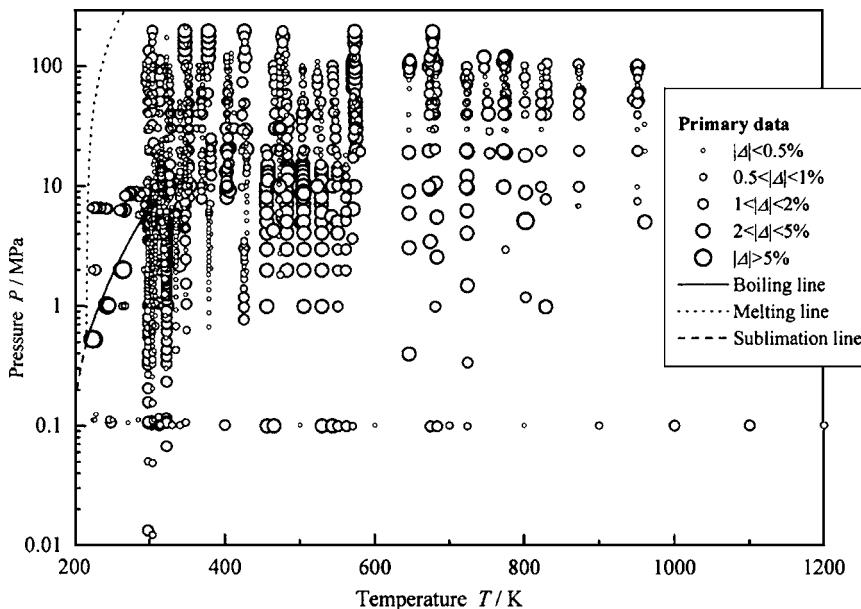


FIG. 3. Deviations between Eq. (7) and the points in the primary data sets.

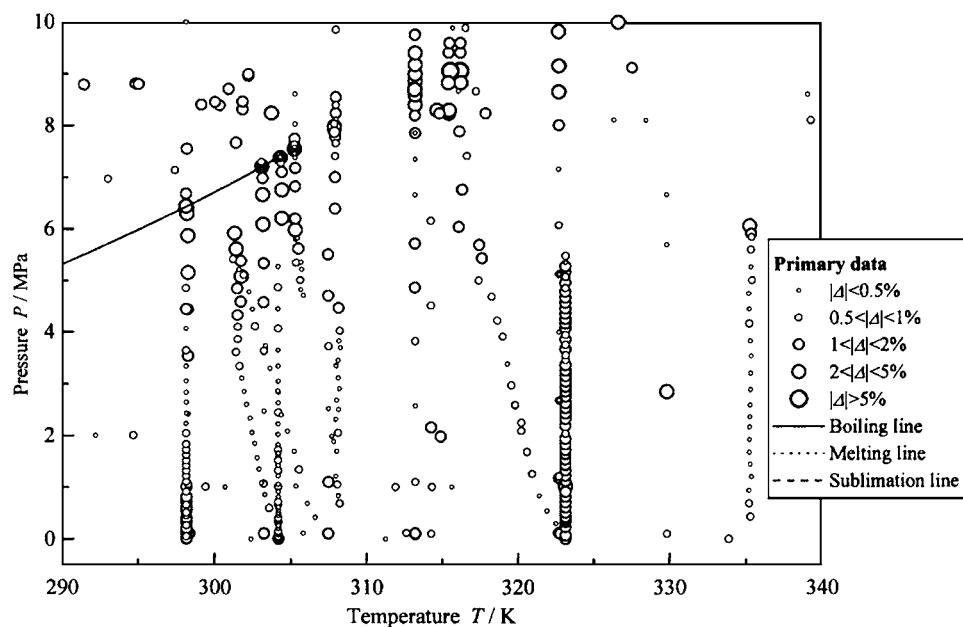


FIG. 4. Deviations between Eq. (7) and the primary data around the critical temperature.

saturated conditions are due to the divergence toward infinity of the thermal conductivity when approaching the critical point. The effect of the critical term contribution can also be noted in the plots of an isotherm and an isobar at temperature or pressure near the respective critical values.

A more detailed representation for the near-critical region is shown in Fig. 8, where some of the experimental data from Michels *et al.*²⁷ are plotted for comparison reporting for each isotherm the points at approximately the same temperature. The good representation of the experimental data confirms the capability of the critical enhancement term, Eqs. (5) and (6), in representing the near-critical behavior of thermal conductivity.

5.5. Discussion on the Validity Limits

The validity limits of the new thermal conductivity equation are stated in Sec. 5.2. It is evident from Fig. 1 that the primary data do not uniformly fill a single regular range, both in temperature and in pressure. For the validity range an irregular contour should be selected for sake of precision. In fact one can see for instance a total lack of data for liquid at $T < 295$ K and $P > 10$ MPa, a scarcity of data for vapor at $T > 400$ K, and $0.1 < P < 1$ MPa, and quite a few points for the region at $T > 700$ K or $P > 100$ MPa. But, looking at the plot reporting sections of the new equation (Fig. 7), it appears that the trends of the new equation, even in the zones where experimental points are not available, are regular and

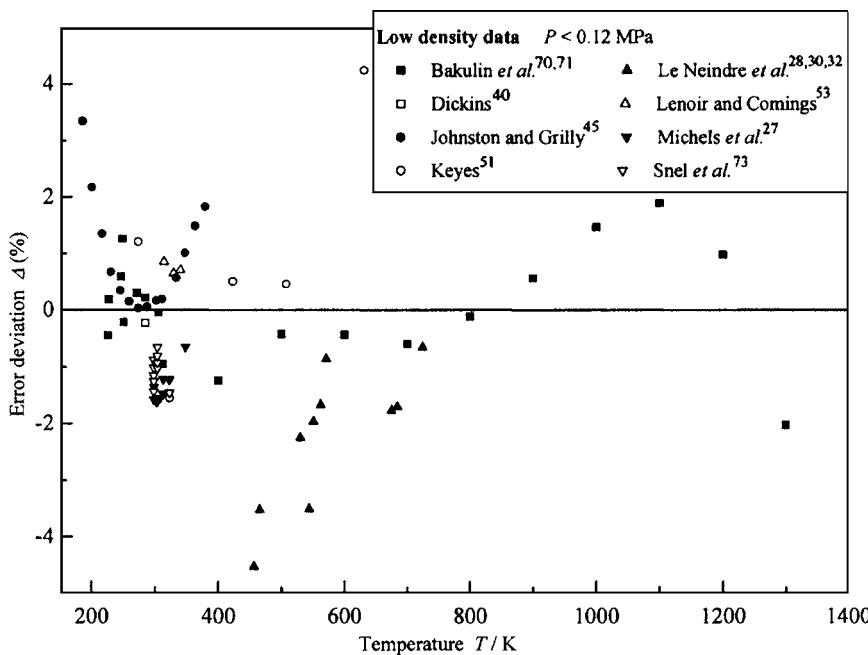


FIG. 5. Deviations between Eq. (7) and the primary experimental points in the low-density region.

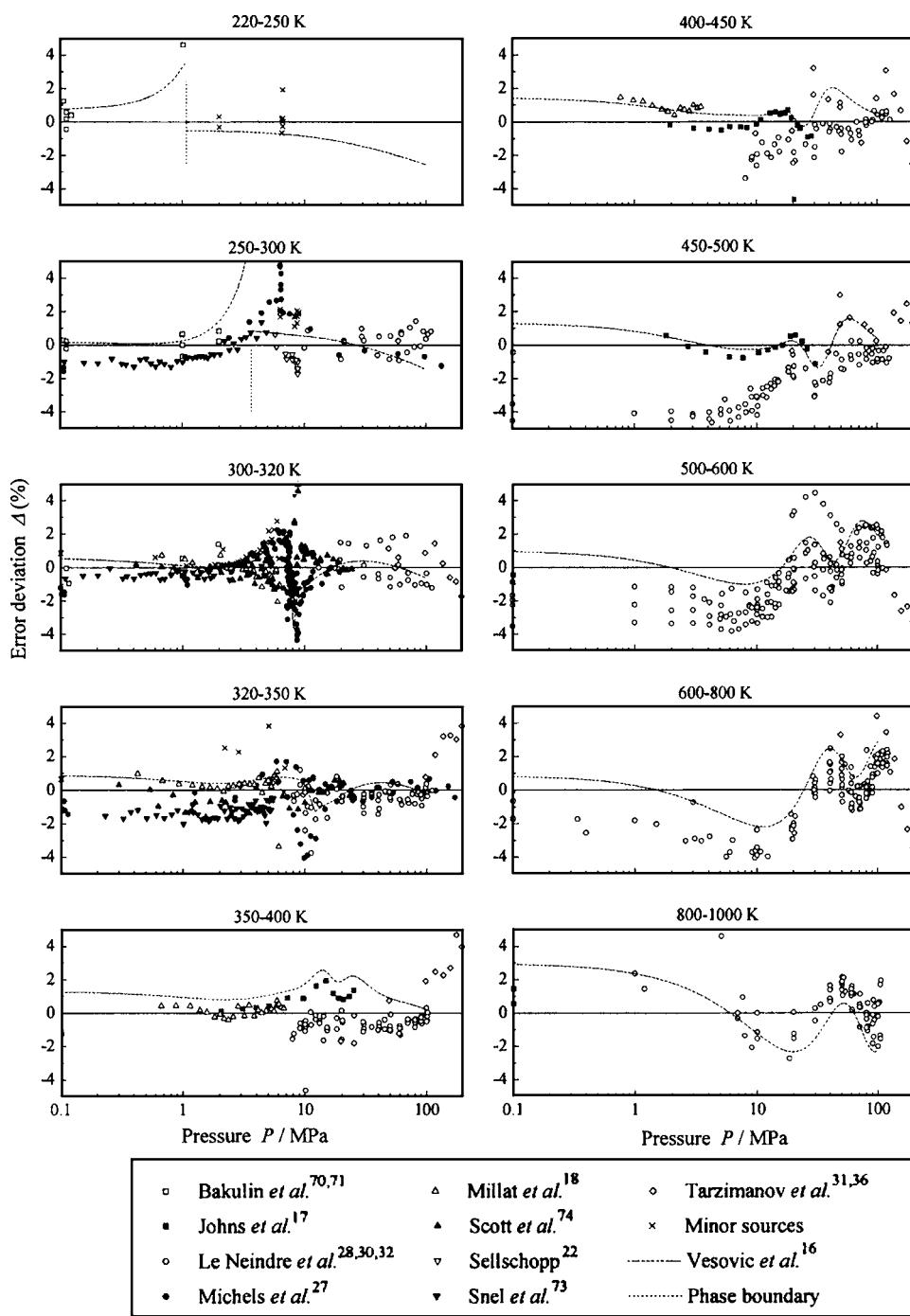


FIG. 6. Deviations of Eq. (7) with respect to all the experimental points in the primary data sets and with respect to the conventional equation¹⁶ as a function of pressure for several intervals of temperature.

agree with the expected behavior. This indicates that the equation could also be used in these zones, but taking into account that there the equation accuracy cannot be verified for lack of experimental data.

Moreover, it should be remembered that in the liquid phase, particularly at high pressures, the effect of a pressure variation on density is quite small (see also Fig. 7). Therefore, since the equation variables are T and ρ , a strong extrapolation in pressure may correspond to a small extrapolation of the thermal conductivity equation. On the other hand,

in the vapor and supercritical regions at high temperatures, the dependence of thermal conductivity on pressure is quite regular and smooth, allowing a reliable behavior of both interpolation and extrapolation. For these reasons the validity range in the T, P plane is taken with a rectangular shape (see Table 5).

However, for the region at temperatures higher than 500 K only experimental sources with lower experimental quality are available from the literature and consequently at those conditions the uncertainty of the equation also increases.

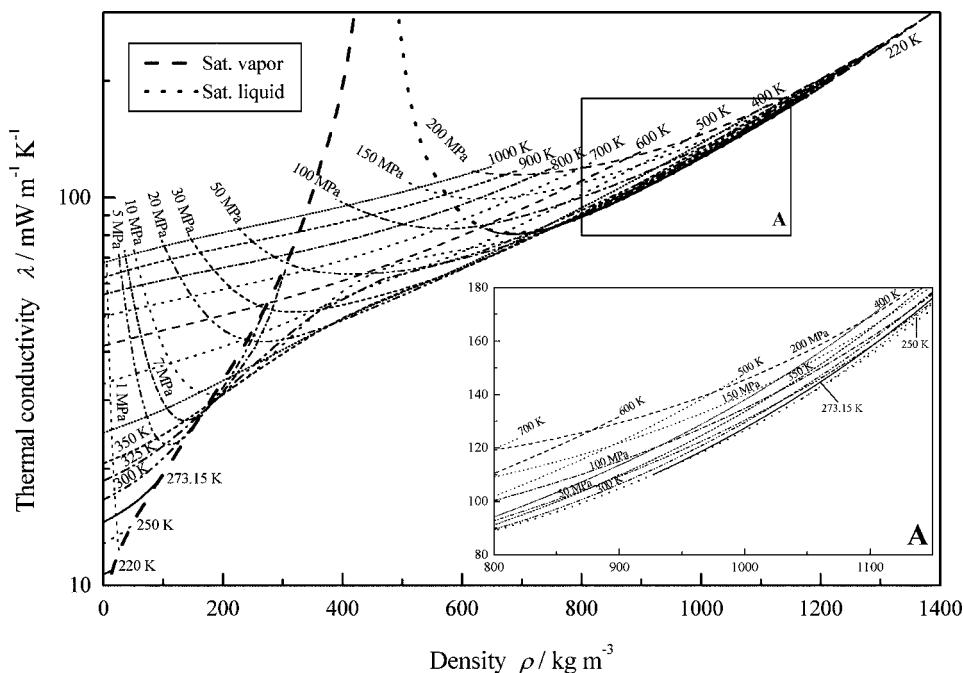


FIG. 7. Representation of Eq. (7) on a λ, ρ plane for some isotherms and isobars.

6. Comparison with the Conventional Equation

The conventional equation from Vesovic *et al.*¹⁶ was used for comparison. In that work the density and the involved thermodynamic properties were calculated by the analytic equation of state from Ely *et al.*,⁸³ except for the critical region where the scaled fundamental equation developed by Albright *et al.*⁸⁴ was used. Therefore the Vesovic *et al.*¹⁶ equation here was coherently applied using the same equations of state from Ely *et al.*⁸³ and Albright *et al.*⁸⁴ for the calculation of the thermodynamic properties required by that conventional equation.

A comparison with the proposed equation is made within the validity limits of the conventional equation, which are somewhat more restricted than the ones of the new equation. The results of the comparison are shown in Table 9.

With respect to primary data the two equations are substantially equivalent in the liquid region; in the vapor phase the AAD values are comparable, but the new equation shows quite a lower value for the bias; in the supercritical region the proposed equation has better values for both AAD and bias.

A graphic comparison between the two equations and with respect to experimental data is reported in Fig. 6. Further-

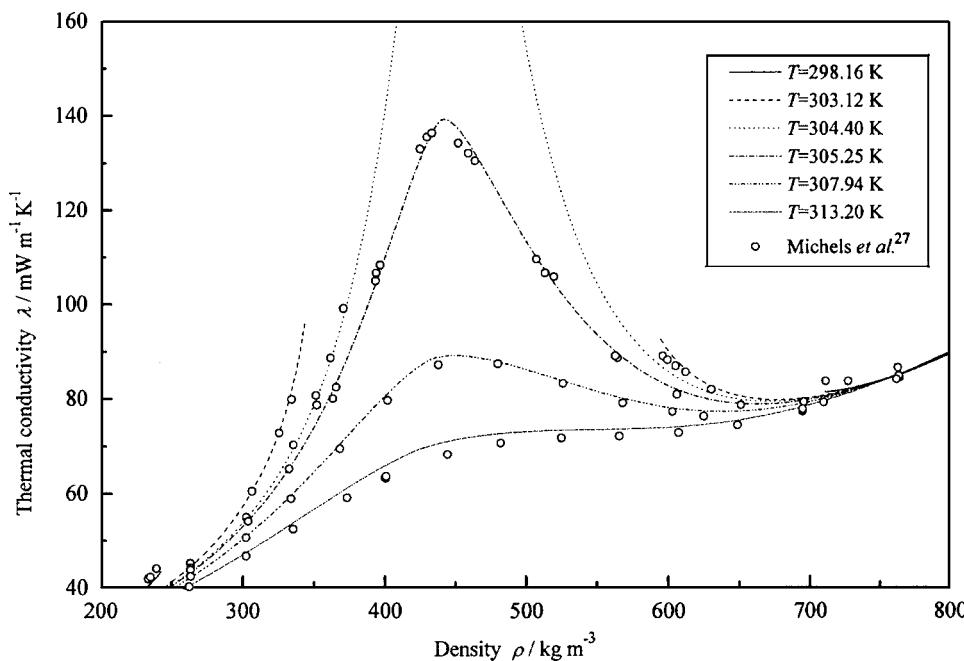


FIG. 8. Representation of Eq. (7) on a λ, ρ plane in the near-critical region.

TABLE 9. Comparison of the performances of the new thermal conductivity equation, Eq. (7), and of the Vesovic *et al.*¹⁶ conventional equation. Data are within the conventional equation validity limits

Ref.	First author	Phase	NPT	Eq. (7)			Vesovic <i>et al.</i> ¹⁶			Class Eq. (7)
				AAD (%)	Bias (%)	MAD (%)	AAD (%)	Bias (%)	MAD (%)	
Liquid phase										
22	Sellschopp	1	22	1.30	-0.68	4.30	1.55	-0.97	4.74	I
27	Michels	1	13	1.39	-0.26	3.12	0.94	-0.27	2.24	I
28	Le Neindre	1	12	0.93	0.93	1.80	1.03	0.99	2.06	I
30	Le Neindre	1	6	0.39	-0.08	1.04	0.35	-0.03	0.95	I
32	Le Neindre	1	9	0.49	-0.41	0.91	0.70	-0.19	1.30	I
34	Salmanov	1	19	1.54	1.47	2.12	1.51	1.51	2.42	I
36	Tarzimanov	1	6	0.66	0.66	1.13	0.69	0.69	1.59	I
Primary		87	1.13	0.24			1.15	0.21		
23	Koch	1	18	1.11	-1.09	3.48	1.58	-1.58	3.23	II
24	Borovik	1	9	2.65	-2.63	6.41	3.08	-3.08	6.15	II
25	Keyes	1	1	1.91	-1.91	1.91	2.60	-2.60	2.60	II
26	Guildner	1	4	2.41	2.41	3.36	1.77	1.77	2.65	II
29	Shingarev	1	17	3.47	-1.26	11.28	3.18	-1.45	10.30	II
31	Tarzimanov	1	4	1.06	-0.99	1.77	0.99	-0.98	2.21	II
33	Paul	1	5	1.83	1.83	3.75	1.30	1.30	2.44	II
35	Becker	1	19	1.98	1.21	5.75	1.76	0.57	5.46	II
23	Koch	sl	8	6.50	-4.78	32.38	6.33	-5.65	31.73	II
37	Amirkhanov	sl	90	8.60	-6.72	46.36	9.51	-7.91	45.64	II
Total		262	4.16	-2.49			4.47	-3.06		
Vapor phase										
40	Dickins	zd	1	0.23	-0.23	0.23	0.52	-0.52	0.52	I
45	Johnston	zd	12	0.65	0.65	1.82	0.26	-0.14	0.47	I
51	Keyes	zd	5	1.59	0.97	4.24	1.72	0.08	3.50	I
53	Lenoir	v	12	1.27	1.24	3.83	0.87	0.66	2.98	I
27	Michels	v	71	1.33	0.57	4.75	0.81	-0.31	2.36	I
30	Le Neindre	v	70	2.85	-2.64	6.26	2.72	-2.55	5.98	I
70	Bakulin	v	28	1.68	1.45	7.46	1.24	0.65	5.26	I
71	Bakulin	v	7	0.69	-0.12	1.46	2.04	-2.04	3.21	I
72	Clifford	v	22	0.83	0.81	2.77	0.17	0.11	0.77	I
73	Snel	v	133	0.92	-0.81	2.03	1.15	-1.15	2.43	I
74	Scott	v	42	0.65	-0.50	1.60	1.04	-1.04	2.50	I
17	Johns	v	14	0.40	-0.03	0.90	0.60	-0.59	0.90	I
18	Millat	v	91	0.50	0.18	3.37	0.65	-0.54	4.19	I
Primary		508	1.17	-0.33			1.16	-0.87		
38	Weber	zd	1	1.56	-1.56	1.56	1.77	-1.77	1.77	II
39	Trautz	zd	1	3.25	-3.25	3.25	3.46	-3.46	3.46	II
41	Kannuluik	zd	1	1.59	-1.59	1.59	1.80	-1.80	1.80	II
22	Sellschopp	v	18	7.01	-7.01	14.18	8.92	-8.92	16.67	II
42	Archer	zd	11	7.12	-7.12	11.13	8.28	-8.28	12.38	II
43	Sherratt	zd	10	1.75	1.48	4.48	1.33	0.31	3.52	II
44	Eucken	zd	5	6.75	-6.75	9.38	7.80	-7.80	10.63	II
23	Koch	v	32	5.91	-5.91	34.75	7.06	-7.06	37.01	II
46	Kannuluik	v	15	1.83	1.76	4.70	1.37	1.12	3.46	II
24	Borovik	v	7	10.26	-10.26	41.98	11.71	-11.71	44.36	II
25	Keyes	v	14	7.66	7.66	20.20	6.61	6.61	17.69	II
47	Stops	zd	4	3.05	-1.75	8.48	4.53	-3.67	9.40	II
48	Kannuluik	v	9	2.06	-2.06	3.60	2.26	-2.26	3.82	II
49	Stolyarov	v	12	4.64	2.61	13.04	3.80	1.72	12.01	II

TABLE 9. Comparison of the performances of the new thermal conductivity equation, Eq. (7), and of the Vesovic *et al.*¹⁶ conventional equation. Data are within the conventional equation validity limits—Continued

Ref.	First author	Phase	NPT	Eq. (7)			Vesovic <i>et al.</i> ¹⁶			Class Eq. (7)
				AAD (%)	Bias (%)	MAD (%)	AAD (%)	Bias (%)	MAD (%)	
50	Franck	zd	6	6.27	-6.27	8.55	7.25	-7.25	9.51	II
52	Keyes	v	9	2.43	1.44	7.14	2.01	0.49	4.97	II
54	Rothman	v	23	3.82	-2.46	7.52	4.16	-4.13	8.28	II
55	Thomas	zd	4	1.33	-1.33	1.49	2.16	-2.16	2.33	II
56	Salceanu	zd	1	6.01	-6.01	6.01	6.55	-6.55	6.55	II
57	Guildner	v	4	1.33	-0.90	2.38	1.94	-1.57	2.76	II
58	Vines	v	2	1.95	1.95	2.32	0.81	0.55	1.36	II
59	Geier	v	8	1.71	-0.08	2.34	2.44	-1.65	6.11	II
26	Guildner	v	12	1.99	-0.89	5.78	2.04	-2.04	3.77	II
27	Michels	v	33	14.40	13.94	59.17	13.93	13.52	58.39	II
60	Westenberg	zd	3	1.57	-1.57	2.03	2.65	-2.65	3.52	II
28	Le Neindre	v	11	0.68	-0.10	1.45	1.57	-1.36	4.20	II
61	Mukhopadhyay	v	7	1.90	-0.82	4.79	2.52	-1.68	5.95	II
62	Barua	zd	5	2.61	-2.10	4.95	3.70	-3.26	6.17	II
63	Christensen	zd	3	1.53	-1.53	1.72	2.54	-2.54	3.16	II
29	Shingarev	v	2	2.04	-2.04	2.58	2.09	-2.09	2.60	II
64	Van Dael	v	1	1.05	-1.05	1.05	1.41	-1.41	1.41	II
30	Le Neindre	v	42	2.33	-2.10	5.02	3.09	-3.00	6.51	II
65	Rosenbaum	v	8	1.07	-1.03	2.72	1.76	-1.76	3.53	II
66	Gupta	v	63	4.26	-4.26	8.72	6.12	-6.12	9.67	II
67	Murthy	v	2	0.59	0.37	0.96	0.57	-0.06	0.63	II
31	Tarzimanov	v	8	2.16	-2.16	3.92	3.58	-3.58	5.39	II
32	Le Neindre	v	37	2.54	-1.69	5.02	3.00	-3.00	6.51	II
68	Haarman	zd	8	0.48	-0.48	0.62	1.80	-1.80	2.05	II
33	Paul	v	12	1.80	0.39	6.46	1.81	-0.48	6.37	II
69	Shashkov	zd	9	1.21	-0.87	3.05	2.00	-2.00	3.74	II
35	Becker	v	27	5.97	-5.83	15.69	6.91	-6.91	16.44	II
36	Tarzimanov	v	12	4.15	3.37	10.53	3.01	1.79	6.50	II
19	Chen	v	19	20.74	15.10	38.24	20.20	14.49	38.13	II
20	Dohrn	v	7	4.18	4.18	5.47	3.38	3.38	4.11	II
21	Heinemann	v	3	4.40	4.40	5.38	3.33	3.33	4.02	II
23	Koch	sv	9	24.11	-23.29	95.99	25.75	-25.75	87.38	II
Total			1048	3.30	-0.62		3.59	-1.48		
Supercritical region										
27	Michels	sc	89	1.28	-0.87	4.37	1.23	0.47	8.81	I
28	Le Neindre	sc	7	0.77	0.72	1.89	0.74	0.58	2.12	I
30	Le Neindre	sc	367	1.22	-0.60	6.41	1.46	-1.14	6.84	I
32	Le Neindre	sc	134	1.02	-0.34	3.90	1.20	-0.77	4.19	I
36	Tarzimanov	sc	33	1.45	1.06	4.41	1.10	-0.06	3.39	I
74	Scott	sc	50	1.15	0.69	6.30	2.43	1.73	10.82	I
17	Johns	sc	33	0.76	0.10	4.65	0.56	-0.40	4.85	I
Primary			713	1.17	-0.38		1.39	-0.57		
22	Sellschopp	sc	10	14.04	10.07	30.07	14.55	11.38	31.13	II
23	Koch	sc	4	40.41	-40.41	102.35	37.77	-37.77	97.88	II
24	Borovik	sc	2	27.38	-27.38	31.77	24.85	-24.85	28.02	II
49	Stolyarov	sc	23	7.71	1.89	20.26	7.34	1.66	19.43	II
53	Lenoir	sc	20	4.65	4.64	9.06	5.25	5.25	10.29	II
57	Guildner	sc	18	12.16	11.01	51.60	13.25	12.77	55.55	II
26	Guildner	sc	1	3.55	3.55	3.55	4.33	4.33	4.33	II
29	Shingarev	sc	4	9.82	-9.82	19.02	9.76	-9.76	18.72	II
65	Rosenbaum	sc	42	2.83	0.13	13.24	3.22	-0.76	12.15	II

TABLE 9. Comparison of the performances of the new thermal conductivity equation, Eq. (7), and of the Vesovic *et al.*¹⁶ conventional equation. Data are within the conventional equation validity limits—Continued

Ref.	First author	Phase	NPT	Eq. (7)			Vesovic <i>et al.</i> ¹⁶			Class Eq. (7)
				AAD (%)	Bias (%)	MAD (%)	AAD (%)	Bias (%)	MAD (%)	
75	Murthy	sc	53	16.96	12.95	42.27	19.22	17.49	43.01	II
67	Murthy	sc	1	0.91	0.91	0.91	2.07	2.07	2.07	II
31	Tarzmanov	sc	48	2.35	-2.15	5.05	3.20	-3.20	5.25	II
76	Murthy	sc	65	13.99	10.72	42.27	16.05	14.64	43.01	II
33	Paul	sc	4	0.78	-0.29	1.69	0.70	0.70	1.46	II
35	Becker	sc	170	9.49	-1.39	54.76	6.16	1.76	44.47	II
19	Chen	sc	47	27.04	25.26	74.05	27.87	25.96	70.70	II
Total				1225	5.43	1.76	5.39	2.50		
Overall										
Primary				1308	1.17	-0.38	1.28	-0.63		
Total				2535	4.41	0.34	4.55	0.28		

more, the deviations of the conventional equation from the primary experimental points are plotted in Figs. 9 and 10, which correspond to Figs. 3 and 4 for the new equation. The behavior of the conventional equation in the near-critical region is shown in Fig. 11 and it can be compared with that of the proposed equation plotted in Fig. 8.

However, apart from limited differences in the performances also depending on the selection of the primary data sets, the behaviors of the two equations with respect to data can be regarded as equivalent. Nevertheless, another element of comparison has to be stressed: from the user's point of view, the conventional equation is quite heavy to implement into computer software. In fact the critical enhancement term of the conventional thermal conductivity equation is extremely complicated: its calculation also requires the viscos-

ity value, the solution of cubic and quartic equations in complex variables, the solution of linear systems with complex coefficients and variables, and the handling of equations with complex parameters. Furthermore, different thermodynamic properties, like density, isobaric and isochoric heat capacities, and isothermal compressibility, are required and they have to be calculated from the EoS. The scaled EoS⁸⁴ itself is very difficult to handle because it implies the solution of a number of implicit equations.

Consequently, apart from calculation speed and numerical stability, in order to overcome these difficulties a user not particularly experienced in numerical methods and in scaled fundamental equations of state could decide to use the simplified equation for the critical enhancement¹⁶ and the Ely *et al.*⁸³ EoS (or the Span and Wagner¹ EoS) all over the T, P

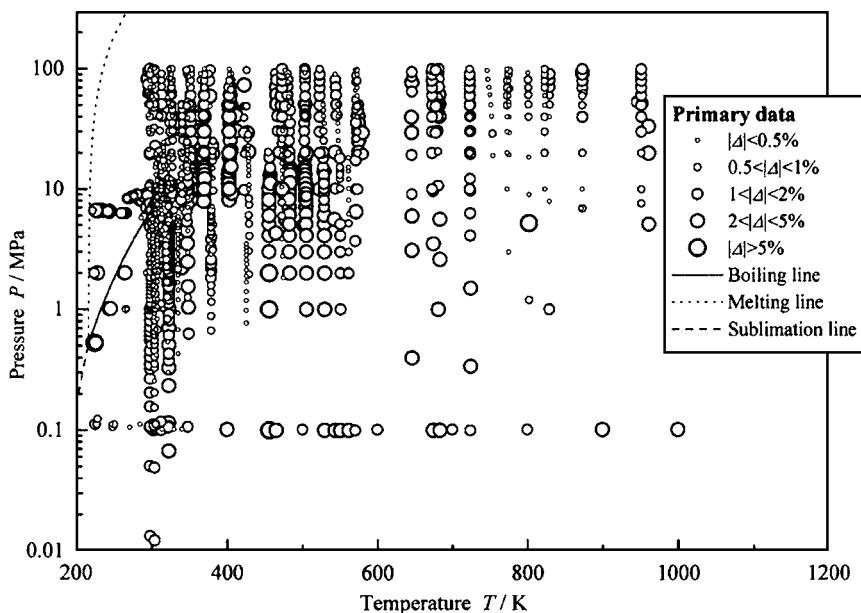


FIG. 9. Deviations between the conventional equation¹⁶ and the points in the primary data sets.

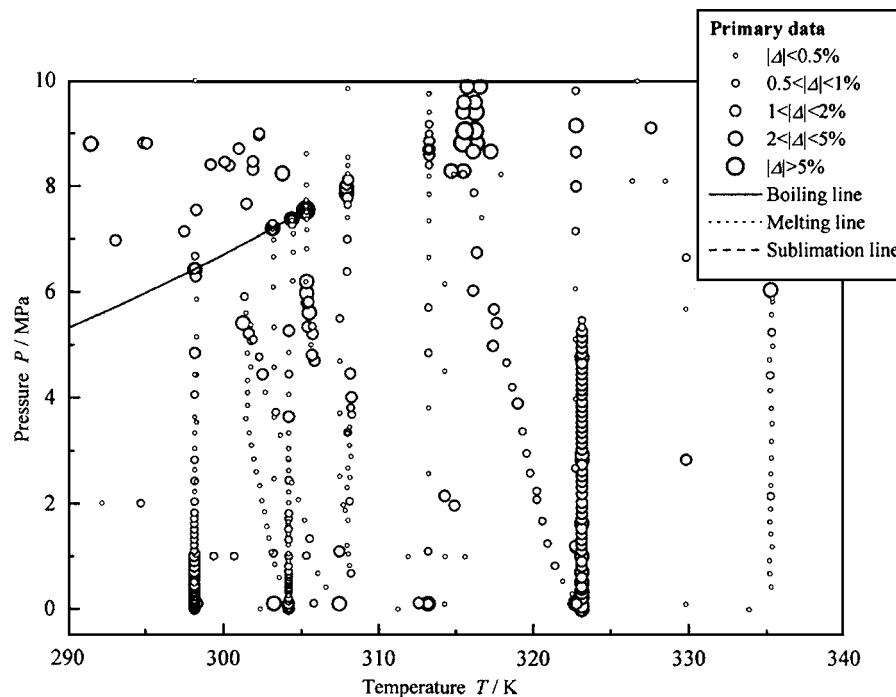


FIG. 10. Deviations between the conventional equation¹⁶ and the primary data around the critical temperature.

plane, as it was done for instance by Lemmon *et al.*⁸⁵ The effect of these simplifications on the accuracy of such an implemented model is not exactly known, even if it can be roughly guessed. In fact Vesovic *et al.*¹⁶ stated that the use of the simplified equation for the critical enhancement, although maintaining the scaled EoS of Albright *et al.*⁸⁴ for the critical region, raises the standard deviation of the Michels *et al.*²⁷ data from 1.5% to 2.7%.

On the contrary, the computer implementation of the thermal conductivity model proposed in the present work is absolutely plain: it is composed of few explicit equations involving basic mathematics and the only required

thermodynamic quantity, i.e., density, can be easily calculated all over the T, P plane from an accurate EoS.¹

7. Tabulations of the Thermal Conductivity Equation

Tabulations of thermal conductivity values of carbon dioxide generated from Eq. (7) are reported in Tables 10 and 11 for the saturation line and the single phase regions, respectively. The density values and the saturation properties are obtained from the EoS of Span and

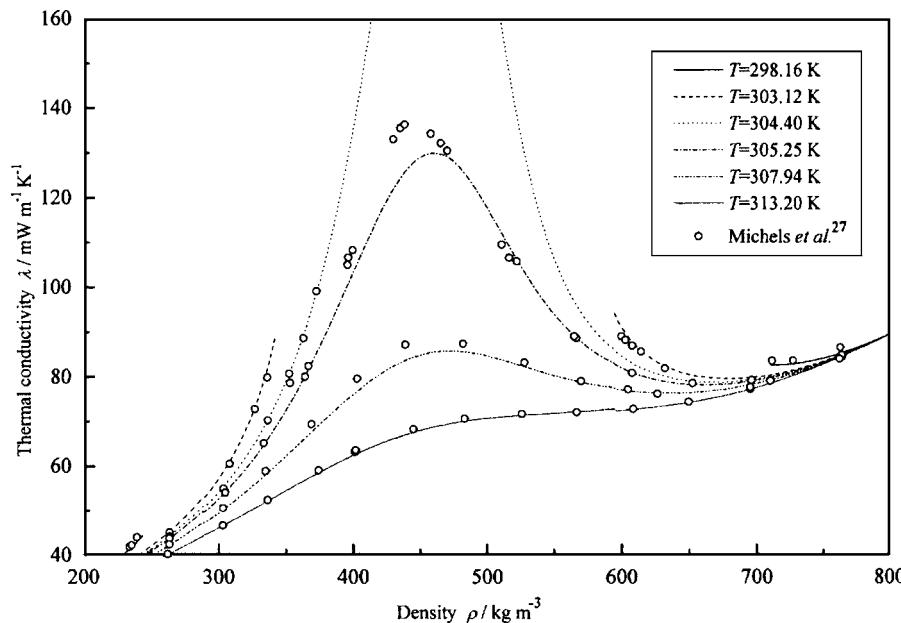


FIG. 11. Representation of the conventional equation on a λ, ρ plane in the near-critical region.

TABLE 10. Thermal conductivity of carbon dioxide along the saturation line. The saturation pressures and the densities are calculated by the EoS of Span and Wagner¹

Temperature (K)	Pressure (MPa)	Saturated liquid		Saturated vapor	
		Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
218.0	0.55042	1173.40	181.09	14.584	10.837
220.0	0.59913	1166.14	178.26	15.817	11.007
222.0	0.65101	1158.81	175.46	17.131	11.180
224.0	0.70621	1151.40	172.69	18.530	11.357
226.0	0.76484	1143.92	169.94	20.016	11.537
228.0	0.82703	1136.34	167.21	21.595	11.721
230.0	0.89291	1128.68	164.51	23.271	11.910
232.0	0.96262	1120.93	161.83	25.050	12.104
234.0	1.0363	1113.08	159.18	26.936	12.303
236.0	1.1141	1105.12	156.54	28.935	12.509
238.0	1.1961	1097.05	153.93	31.052	12.721
240.0	1.2825	1088.87	151.33	33.295	12.942
242.0	1.3734	1080.56	148.76	35.670	13.173
244.0	1.4690	1072.13	146.20	38.184	13.414
246.0	1.5693	1063.56	143.65	40.845	13.669
248.0	1.6746	1054.84	141.13	43.662	13.939
250.0	1.7850	1045.97	138.61	46.644	14.227
252.0	1.9007	1036.93	136.11	49.801	14.542
254.0	2.0217	1027.72	133.62	53.144	14.845
256.0	2.1483	1018.32	131.14	56.685	15.162
258.0	2.2806	1008.71	128.68	60.438	15.501
260.0	2.4188	998.89	126.21	64.417	15.865
262.0	2.5630	988.83	123.76	68.640	16.255
264.0	2.7134	978.51	121.31	73.124	16.676
266.0	2.8701	967.92	118.87	77.891	17.132
268.0	3.0334	957.04	116.43	82.965	17.627
270.0	3.2033	945.83	113.99	88.374	18.168
272.0	3.3802	934.26	111.55	94.148	18.762
274.0	3.5642	922.30	109.11	100.32	19.417
276.0	3.7555	909.90	106.68	106.95	20.143
278.0	3.9542	897.02	104.24	114.07	20.952
280.0	4.1607	883.58	101.80	121.74	21.861
282.0	4.3752	869.52	99.359	130.05	22.888
284.0	4.5978	854.74	96.920	139.09	24.059
286.0	4.8289	839.12	94.487	148.98	25.409
288.0	5.0688	822.50	92.066	159.87	26.985
290.0	5.3177	804.67	89.673	171.96	28.855
292.0	5.5761	785.33	87.334	185.55	31.123
294.0	5.8443	764.09	85.100	201.06	33.962
296.0	6.1227	740.28	83.074	219.14	37.680
298.0	6.4121	712.77	81.485	240.90	42.908
300.0	6.7131	679.24	80.957	268.58	51.240
302.0	7.0268	633.69	83.968	308.15	68.705
304.0	7.3555	530.30	140.30	406.42	217.95

Wagner.¹ These tables can also provide useful reference values in the validation of a computer code for the calculation procedure.

8. Conclusions

A completely correlative modeling method was adopted for the development of a new thermal conductivity equation

for carbon dioxide, for which a former conventional equation¹⁶ was available. The technique is based on the optimization method for the functional form of multiparameter equations of state, set up by Setzmann and Wagner¹⁵, and it is combined with a nonlinear method. Such a function approximator was applied to the available thermal conductivity data of the target fluid. An analytical expression able to ac-

TABLE 11. Thermal conductivity of carbon dioxide in the single phase regions. The densities are calculated by the EoS of Span and Wagner¹

Temperature	225 K		250 K		275 K	
	Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)
0.01	0.23555	11.037	0.21191	12.849	0.19260	14.727
0.05	1.1837	11.057	1.0634	12.870	0.96552	14.748
0.10	2.3828	11.081	2.1363	12.896	1.9374	14.776
0.15	3.5977	11.107	3.2191	12.922	2.9157	14.803
0.20	4.8292	11.132	4.3120	12.949	3.9006	14.831
0.25	6.0779	11.159	5.4153	12.976	4.8921	14.859
0.30	7.3445	11.185	6.5292	13.003	5.8905	14.888
0.40	9.9347	11.240	8.7902	13.060	7.9081	14.946
0.50	12.607	11.298	11.097	13.118	9.9545	15.006
0.60	15.369	11.359	13.454	13.179	12.031	15.067
0.80	1147.83	171.37	18.326	13.308	16.278	15.194
1.00	1148.32	171.56	23.435	13.450	20.660	15.330
1.50	1149.53	172.03	37.509	13.898	32.288	15.718
2.00	1150.73	172.50	1046.88	138.88	45.090	16.204
2.50	1151.92	172.97	1048.97	139.51	59.448	16.845
3.00	1153.10	173.43	1051.02	140.12	76.011	17.744
4.00	1155.43	174.35	1055.01	141.33	919.56	108.61
5.00	1157.72	175.26	1058.86	142.51	928.78	110.58
6.00	1159.97	176.16	1062.59	143.66	937.12	112.41
7.00	1162.17	177.05	1066.20	144.79	944.77	114.13
8.00	1164.35	177.93	1069.70	145.89	951.86	115.75
9.00	1166.48	178.80	1073.11	146.97	958.48	117.30
10.00	1168.59	179.66	1076.42	148.04	964.71	118.78
15.00	1178.64	183.84	1091.77	153.08	991.45	125.43
20.00	1188.00	187.84	1105.47	157.77	1013.23	131.21
25.00	1196.78	191.68	1117.90	162.17	1031.80	136.42
30.00	1205.06	195.39	1129.30	166.34	1048.09	141.21
40.00	1220.33	202.44	1149.68	174.11	1075.88	149.87
50.00	1234.21	209.10	1167.59	181.31	1099.22	157.65
60.00	1246.96	215.44	1183.63	188.05	1119.48	164.82
70.00	1258.77	221.51	1198.21	194.43	1137.45	171.51
80.00	1269.80	227.35	1211.60	200.50	1153.65	177.82
100.00	1289.91	238.44	1235.57	211.94	1182.06	189.56
150.00	1332.10	263.68	1284.39	237.60	1238.14	215.51
200.00	1366.64	286.50	1323.31	260.52	1281.64	238.44
Temperature	300 K		325 K		350 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
0.01	0.17652	16.659	0.16293	18.637	0.15128	20.652
0.05	0.88434	16.681	0.81585	18.657	0.75726	20.671
0.10	1.7730	16.708	1.6348	18.683	1.5167	20.695
0.15	2.6661	16.736	2.4568	18.710	2.2784	20.719
0.20	3.5636	16.764	3.2819	18.736	3.0423	20.743
0.25	4.4657	16.793	4.1101	18.762	3.8085	20.767
0.30	5.3723	16.821	4.9416	18.788	4.5770	20.791
0.40	7.1994	16.879	6.6141	18.841	6.1207	20.839
0.50	9.0456	16.937	8.2996	18.895	7.6736	20.887
0.60	10.911	16.997	9.9985	18.949	9.2360	20.936
0.80	14.703	17.120	13.437	19.060	12.389	21.034
1.00	18.579	17.248	16.932	19.173	15.581	21.133
1.50	28.674	17.599	25.930	19.474	23.739	21.390
2.00	39.420	18.006	35.333	19.806	32.165	21.663
2.50	50.936	18.492	45.186	20.180	40.878	21.957

TABLE 11. Thermal conductivity of carbon dioxide in the single phase regions. The densities are calculated by the EoS of Span and Wagner¹—Continued

Temperature		300 K		325 K		350 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)		Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
3.00	63.376	19.083		55.544	20.607	49.901	22.279
4.00	91.965	20.759		78.043	21.677	68.976	23.031
5.00	128.40	23.635		103.53	23.156	89.619	23.971
6.00	182.31	29.773		133.08	25.240	112.12	25.155
7.00	706.06	80.915		168.48	28.230	136.82	26.637
8.00	753.17	84.071		212.90	32.660	164.16	28.474
9.00	780.97	87.110		272.52	39.616	194.63	30.719
10.00	801.62	89.783		358.04	50.703	228.80	33.433
15.00	865.82	99.977		683.09	76.055	449.20	53.133
20.00	905.57	107.58		773.46	86.518	614.18	67.117
25.00	935.42	113.93		825.55	94.397	702.22	77.030
30.00	959.70	119.50		862.99	100.92	758.98	84.813
40.00	998.35	129.19		917.21	111.72	833.72	96.943
50.00	1028.94	137.61		957.10	120.76	884.76	106.63
60.00	1054.48	145.20		989.03	128.72	923.92	114.95
70.00	1076.54	152.17		1015.81	135.94	955.90	122.38
80.00	1096.02	158.69		1038.99	142.62	983.05	129.17
100.00	1129.45	170.68		1077.91	154.79	1027.73	141.45
150.00	1193.37	196.80		1150.09	180.96	1108.35	167.54
200.00	1241.61	219.64		1203.16	203.64	1166.27	189.98
Temperature		375 K		400 K		425 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)		Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
0.01	0.14118	22.697		0.13235	24.764	0.12456	26.845
0.05	0.70656	22.716		0.66224	24.782	0.62317	26.863
0.10	1.4147	22.739		1.3257	24.805	1.2472	26.886
0.15	2.1245	22.761		1.9903	24.828	1.8722	26.909
0.20	2.8360	22.784		2.6562	24.850	2.4981	26.931
0.25	3.5490	22.807		3.3233	24.873	3.1249	26.954
0.30	4.2638	22.830		3.9916	24.895	3.7526	26.976
0.40	5.6982	22.876		5.3318	24.940	5.0107	27.021
0.50	7.1393	22.921		6.6770	24.985	6.2725	27.066
0.60	8.5871	22.967		8.0271	25.030	7.5380	27.111
0.80	11.503	23.059		10.742	25.120	10.080	27.200
1.00	14.447	23.151		13.477	25.210	12.637	27.289
1.50	21.931	23.385		20.405	25.435	19.094	27.510
2.00	29.601	23.628		27.464	25.664	25.647	27.732
2.50	37.464	23.882		34.658	25.900	32.296	27.957
3.00	45.530	24.151		41.992	26.144	39.043	28.187
4.00	62.313	24.750		57.094	26.667	52.838	28.666
5.00	80.038	25.452		72.804	27.253	67.044	29.183
6.00	98.799	26.281		89.155	27.916	81.670	29.748
7.00	118.70	27.260		106.18	28.668	96.725	30.368
8.00	139.84	28.403		123.90	29.515	112.21	31.049
9.00	162.33	29.717		142.35	30.460	128.13	31.792
10.00	186.24	31.209		161.53	31.504	144.47	32.596
15.00	326.31	41.505		267.42	38.172	231.75	37.495
20.00	471.78	53.688		380.50	47.071	323.66	43.948
25.00	580.03	63.216		481.55	55.418	411.09	51.129
30.00	654.38	71.388		561.50	62.411	487.13	57.354
40.00	750.62	84.561		672.08	74.852	602.30	68.022
50.00	813.55	94.860		745.45	85.295	682.49	77.812
60.00	860.29	103.50		799.32	94.104	742.12	86.494

TABLE 11. Thermal conductivity of carbon dioxide in the single phase regions. The densities are calculated by the EoS of Span and Wagner¹—Continued

Temperature		375 K		400 K		425 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)		Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
70.00	897.61	111.09		841.76	101.79	789.03	94.161
80.00	928.79	117.98		876.80	108.71	827.56	101.05
100.00	979.26	130.29		932.81	120.98	888.67	113.23
150.00	1068.23	156.18		1029.80	146.58	993.12	138.47
200.00	1130.90	178.33		1097.04	168.38	1064.66	159.89
Temperature		450 K		475 K		500 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)		Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
0.01	0.11764	28.933		0.11144	31.020	0.10587	33.101
0.05	0.58847	28.951		0.55743	31.039	0.52951	33.119
0.10	1.1776	28.974		1.1154	31.062	1.0594	33.143
0.15	1.7674	28.997		1.6738	31.084	1.5897	33.166
0.20	2.3580	29.019		2.2328	31.107	2.1204	33.189
0.25	2.9491	29.042		2.7923	31.130	2.6514	33.212
0.30	3.5410	29.065		3.3523	31.153	3.1829	33.235
0.40	4.7268	29.110		4.4739	31.198	4.2470	33.280
0.50	5.9154	29.155		5.5975	31.243	5.3126	33.325
0.60	7.1067	29.199		6.7232	31.288	6.3798	33.371
0.80	9.4975	29.288		8.9808	31.377	8.5189	33.460
1.00	11.899	29.377		11.247	31.466	10.664	33.548
1.50	17.952	29.596		16.947	31.684	16.054	33.766
2.00	24.075	29.814		22.699	31.899	21.482	33.980
2.50	30.268	30.032		28.502	32.112	26.948	34.191
3.00	36.531	30.251		34.357	32.325	32.451	34.400
4.00	49.270	30.701		46.218	32.754	43.566	34.815
5.00	62.295	31.172		58.281	33.193	54.826	35.231
6.00	75.605	31.671		70.542	33.648	66.223	35.654
7.00	89.200	32.206		82.996	34.123	77.753	36.087
8.00	103.07	32.779		95.637	34.622	89.410	36.533
9.00	117.22	33.392		108.46	35.145	101.19	36.994
10.00	131.63	34.044		121.45	35.694	113.07	37.470
15.00	207.01	37.872		188.44	38.806	173.76	40.077
20.00	285.14	42.726		256.99	42.595	235.24	43.127
25.00	361.01	48.580		324.00	47.269	295.46	46.866
30.00	430.25	54.318		386.66	52.366	352.51	51.231
40.00	542.98	63.700		493.67	61.103	452.94	59.505
50.00	626.20	72.295		576.97	68.544	534.42	66.195
60.00	689.59	80.461		642.26	75.881	600.13	72.623
70.00	739.96	87.936		694.91	82.946	654.00	79.083
80.00	781.42	94.736		738.59	89.547	699.16	85.351
100.00	847.00	106.78		807.90	101.38	771.37	96.884
150.00	958.22	131.62		925.10	125.82	893.75	120.91
200.00	1033.74	152.63		1004.26	146.43	976.16	141.12
Temperature		525 K		550 K		575 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)		Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)
0.01	0.10083	35.169		0.096243	37.218	0.092058	39.243
0.05	0.50426	35.187		0.48130	37.237	0.46035	39.262
0.10	1.0088	35.211		0.96283	37.260	0.92087	39.286
0.15	1.5137	35.234		1.4446	37.284	1.3816	39.309
0.20	2.0188	35.257		1.9265	37.307	1.8424	39.333

TABLE 11. Thermal conductivity of carbon dioxide in the single phase regions. The densities are calculated by the EoS of Span and Wagner¹—Continued

Temperature		525 K		550 K		575 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	
0.25	2.5242	35.280	2.4087	37.331	2.3034	39.357	
0.30	3.0299	35.303	2.8911	37.354	2.7646	39.380	
0.40	4.0423	35.349	3.8566	37.400	3.6874	39.427	
0.50	5.0558	35.395	4.8229	37.446	4.6108	39.473	
0.60	6.0704	35.440	5.7901	37.492	5.5349	39.519	
0.80	8.1032	35.530	7.7271	37.582	7.3850	39.610	
1.00	10.141	35.619	9.6675	37.672	9.2375	39.701	
1.50	15.254	35.838	14.533	37.891	13.880	39.921	
2.00	20.396	36.051	19.419	38.105	18.536	40.136	
2.50	25.565	36.260	24.326	38.314	23.208	40.346	
3.00	30.761	36.467	29.252	38.519	27.893	40.550	
4.00	41.233	36.872	39.160	38.919	37.302	40.948	
5.00	51.807	37.273	49.140	39.310	46.761	41.332	
6.00	62.477	37.674	59.186	39.695	56.264	41.707	
7.00	73.239	38.077	69.294	40.078	65.807	42.076	
8.00	84.085	38.486	79.458	40.460	75.385	42.439	
9.00	95.010	38.902	89.672	40.843	84.993	42.799	
10.00	106.01	39.325	99.930	41.228	94.626	43.156	
15.00	161.74	41.567	151.63	43.201	142.97	44.931	
20.00	217.77	44.083	203.30	45.322	191.06	46.757	
25.00	272.64	47.109	253.87	47.806	238.08	48.827	
30.00	325.03	50.771	302.37	50.857	283.31	51.368	
40.00	419.10	58.492	390.67	57.898	366.46	57.663	
50.00	497.78	64.819	466.18	64.059	438.78	63.684	
60.00	562.86	70.490	529.96	69.236	500.89	68.610	
70.00	617.13	76.251	584.01	74.332	554.27	73.175	
80.00	663.12	82.058	630.31	79.594	600.50	77.882	
100.00	737.38	93.148	705.86	90.089	676.71	87.649	
150.00	864.10	116.74	836.09	113.20	809.65	110.19	
200.00	949.42	136.59	923.96	132.71	899.74	129.40	
Temperature		600 K		650 K		700 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	
0.01	0.088221	41.239	0.081434	45.126	0.075616	48.848	
0.05	0.441115	41.258	0.40719	45.145	0.37809	48.868	
0.10	0.88242	41.282	0.81444	45.170	0.75619	48.893	
0.15	1.3238	41.306	1.2217	45.194	1.1343	48.917	
0.20	1.7653	41.330	1.6291	45.218	1.5124	48.942	
0.25	2.2069	41.354	2.0365	45.243	1.8906	48.967	
0.30	2.6487	41.377	2.4439	45.267	2.2687	48.992	
0.40	3.5325	41.424	3.2590	45.315	3.0250	49.041	
0.50	4.4168	41.471	4.0743	45.363	3.7814	49.089	
0.60	5.3015	41.518	4.8897	45.410	4.5378	49.138	
0.80	7.0723	41.610	6.5212	45.504	6.0507	49.234	
1.00	8.8449	41.701	8.1535	45.597	7.5638	49.329	
1.50	13.284	41.923	12.237	45.824	11.347	49.561	
2.00	17.733	42.140	16.325	46.044	15.130	49.786	
2.50	22.193	42.350	20.417	46.258	18.914	50.005	
3.00	26.661	42.555	24.513	46.466	22.697	50.218	
4.00	35.625	42.952	32.712	46.867	30.262	50.627	
5.00	44.621	43.333	40.921	47.248	37.823	51.015	
6.00	53.645	43.702	49.136	47.614	45.377	51.386	
7.00	62.694	44.061	57.354	47.965	52.922	51.739	

TABLE 11. Thermal conductivity of carbon dioxide in the single phase regions. The densities are calculated by the EoS of Span and Wagner¹—Continued

Temperature		600 K		650 K		700 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	
8.00	71.762	44.412	65.573	48.304	60.457	52.078	
9.00	80.846	44.756	73.789	48.631	67.979	52.402	
10.00	89.941	45.094	81.999	48.948	75.486	52.713	
15.00	135.43	46.724	122.86	50.403	112.72	54.098	
20.00	180.50	48.327	163.12	51.717	149.27	55.268	
25.00	224.54	50.079	202.40	53.040	184.90	56.348	
30.00	266.99	52.207	240.36	54.571	219.39	57.511	
40.00	345.60	57.753	311.36	58.779	284.29	60.692	
50.00	414.84	63.575	375.06	63.974	343.27	65.096	
60.00	475.12	68.409	431.61	68.763	396.36	69.723	
70.00	527.55	72.619	481.74	72.714	444.05	73.715	
80.00	573.40	76.826	526.29	76.255	486.96	77.045	
100.00	649.77	85.783	601.91	83.612	560.93	83.204	
150.00	784.69	107.64	738.93	103.69	698.17	101.07	
200.00	876.69	126.56	833.86	122.08	795.00	118.86	
Temperature		750 K		800 K		850 K	
Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	
0.01	0.070575	52.383	0.066164	55.720	0.062271	58.858	
0.05	0.35287	52.404	0.33081	55.741	0.31134	58.879	
0.10	0.70572	52.429	0.66158	55.767	0.62264	58.906	
0.15	1.0586	52.454	0.99233	55.793	0.93390	58.932	
0.20	1.4114	52.480	1.3230	55.819	1.2451	58.958	
0.25	1.7642	52.505	1.6537	55.845	1.5563	58.985	
0.30	2.1170	52.530	1.9844	55.870	1.8674	59.011	
0.40	2.8226	52.580	2.6456	55.921	2.4896	59.063	
0.50	3.5281	52.630	3.3067	55.972	3.1116	59.115	
0.60	4.2335	52.680	3.9676	56.023	3.7334	59.167	
0.80	5.6442	52.778	5.2892	56.123	4.9765	59.269	
1.00	7.0546	52.875	6.6102	56.222	6.2190	59.371	
1.50	10.579	53.112	9.9104	56.466	9.3220	59.621	
2.00	14.102	53.343	13.207	56.703	12.421	59.864	
2.50	17.622	53.568	16.500	56.934	15.515	60.102	
3.00	21.140	53.787	19.789	57.159	18.604	60.334	
4.00	28.168	54.207	26.355	57.593	24.769	60.782	
5.00	35.184	54.606	32.904	58.006	30.913	61.211	
6.00	42.185	54.987	39.435	58.400	37.036	61.620	
7.00	49.171	55.349	45.945	58.775	43.138	62.011	
8.00	56.139	55.695	52.435	59.134	49.217	62.386	
9.00	63.089	56.026	58.904	59.477	55.272	62.745	
10.00	70.019	56.341	65.349	59.804	61.304	63.088	
15.00	104.32	57.725	97.199	61.232	91.077	64.591	
20.00	137.90	58.845	128.34	62.367	120.15	65.785	
25.00	170.61	59.808	158.65	63.299	148.45	66.745	
30.00	202.31	60.760	188.05	64.149	175.92	67.573	
40.00	262.24	63.221	243.83	66.147	228.18	69.309	
50.00	317.20	66.852	295.34	69.124	276.69	71.788	
60.00	367.18	71.137	342.56	72.966	321.46	75.171	
70.00	412.53	75.179	385.75	76.946	362.68	78.978	
80.00	453.73	78.567	425.28	80.467	400.64	82.590	
100.00	525.63	84.116	494.96	85.909	468.08	88.231	
150.00	661.81	99.605	629.28	99.219	600.07	99.823	
200.00	759.66	116.63	727.46	115.23	698.04	114.57	

TABLE 11. Thermal conductivity of carbon dioxide in the single phase regions. The densities are calculated by the EoS of Span and Wagner¹—Continued

Temperature	900 K		950 K		1000 K	
	Pressure (MPa)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)	Therm. cond. (mW m ⁻¹ K ⁻¹)	Density (kg m ⁻³)
0.01	0.058812	61.808	0.055716	64.594	0.052930	67.258
0.05	0.29404	61.829	0.27856	64.616	0.26463	67.280
0.10	0.58803	61.856	0.55707	64.644	0.52921	67.308
0.15	0.88198	61.883	0.83553	64.671	0.79373	67.336
0.20	1.1759	61.910	1.1139	64.699	1.0582	67.364
0.25	1.4697	61.937	1.3923	64.726	1.3226	67.392
0.30	1.7635	61.964	1.6706	64.753	1.5870	67.420
0.40	2.3510	62.017	2.2271	64.808	2.1156	67.475
0.50	2.9383	62.070	2.7833	64.862	2.6439	67.530
0.60	3.5254	62.123	3.3394	64.916	3.1721	67.585
0.80	4.6989	62.228	4.4509	65.023	4.2278	67.695
1.00	5.8718	62.332	5.5615	65.129	5.2826	67.804
1.50	8.8004	62.588	8.3345	65.391	7.9159	68.072
2.00	11.724	62.838	11.102	65.648	10.544	68.335
2.50	14.643	63.082	13.865	65.899	13.166	68.593
3.00	17.556	63.322	16.622	66.146	15.783	68.847
4.00	23.367	63.785	22.119	66.625	21.001	69.341
5.00	29.156	64.229	27.595	67.086	26.196	69.818
6.00	34.924	64.655	33.047	67.529	31.368	70.279
7.00	40.668	65.064	38.477	67.956	36.517	70.724
8.00	46.389	65.457	43.883	68.368	41.644	71.155
9.00	52.086	65.834	49.265	68.764	46.746	71.571
10.00	57.759	66.195	54.623	69.146	51.825	71.973
15.00	85.740	67.793	81.037	70.847	76.856	73.784
20.00	113.04	69.075	106.80	72.236	101.27	75.287
25.00	139.62	70.105	131.89	73.362	125.04	76.523
30.00	165.44	70.965	156.26	74.292	148.15	77.548
40.00	214.66	72.594	202.83	75.926	192.37	79.265
50.00	260.55	74.726	246.41	77.846	233.89	81.081
60.00	303.13	77.697	287.02	80.482	272.73	83.465
70.00	342.55	81.261	324.80	83.780	309.01	86.508
80.00	379.04	84.883	359.93	87.336	342.88	89.946
100.00	444.32	90.845	423.15	93.612	404.15	96.464
150.00	573.72	101.31	549.85	103.55	528.11	106.39
200.00	671.10	114.60	646.36	115.30	623.57	116.65

curately represent the critical enhancement of thermal conductivity was set up and included in the equation.

The new multiparameter thermal conductivity equation presents an AAD value of 1.19% for the selected 1407 primary data. The performance comparison with the conventional equation on the same data base shows that the two models have similar behaviors, with a slight advantage for the present one. However, the new equation is easier to use and to implement into computer software; moreover it is based on the most recent and precise equation of state for carbon dioxide.

The functional form optimization procedure by Setzmann and Wagner is then a useful tool for the development of thermal conductivity equations for pure fluids since it is capable of representing the thermal conductivity surface within the uncertainty of the experimental data all over the T, P plane.

In order to check and improve the accuracy of the equation, additional experimental data for the thermal conductivity of carbon dioxide would be mainly needed for the liquid phase at $T < 295$ K, for the vapor phase at $T > 400$ K and $0.1 < P < 1$ MPa, and for the regions at high temperatures and high pressures.

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